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University of Cambridge

ELECTRON EMISSION  
AND  
ADSORPTION PHENOMENA

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# ELECTRON EMISSION AND ADSORPTION PHENOMENA

By

J. H. DE BOER

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Translated from the manuscript by

MRS H. E. TEVES-ACLY

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## PREFACE

THIS BOOK owes its existence in the first instance to a conversation with Professor E. K. Rideal during his visit to the Physical Laboratory of the N. V. Philips' Gloeilampenfabrieken in Eindhoven in March 1933. Professor Rideal expressed the desire for a book, written from the physical-chemical point of view, which should show what light can be thrown upon the subject of the adsorption on surfaces by the study of the phenomena of electron emission, and, *vice versa*, what insight into the phenomena of electron emission can be gained from a study of the phenomena of adsorption on surfaces. When he asked me to write such a book and to allow it to be published in the *Cambridge Series of Physical Chemistry*, of which he is the editor, I hesitated at first to accept the honour. The intention was that the book not merely should give a description of phenomena, but especially that it should present a satisfactory interpretation of them from the molecular point of view. At that time I had gained what was to me, at least, tentatively a satisfactory insight into the photoelectric and thermal emission of electrons from dielectric surfaces upon which alkali or alkaline earth metal atoms are adsorbed; such was not the case with adsorption on metals. In the course of the following months, however, it appeared possible here also to reach a satisfactory concept by a comparison of the photoelectric phenomena and the thermionic phenomena in the adsorption on metals, building to some extent on what had been learned from dielectrics. I trust that the complete picture obtained in this way will prove satisfactory, and I hope, moreover, that it will be a stimulant to further research on the subject.

The writing of the book has been very much facilitated by the use of potential curves to represent visually the relations between adsorbed atoms and ions and their adsorption energies. Throughout the whole book this method of representation has been made use of.

The first two chapters are to be regarded more or less as introductory; the first concerns emission phenomena, the



second adsorption. The next four chapters are devoted mainly to the influence on the emission of conduction electrons by adsorption on metal surfaces. In the second part of the book the individual properties of adsorbed atoms are more emphasized. In order to obtain a good insight into the selective photoelectric emission a somewhat more detailed treatment of the absorption of light by matter in the gaseous state (Chap. VII) and in the adsorbed state (Chap. VIII) is necessary. The photoelectric phenomena of internally adsorbed atoms (photoelectric conduction) and the thermal ionization of such atoms (semi-conduction) in Chaps. X, XI and XII correspond completely to the analogous phenomena of atoms adsorbed on external surfaces (Chaps. IX, XIII and XIV). Both types of phenomena are dealt with in Chap. XV.

In all the activities connected with the writing of this book I have experienced whole-hearted cooperation from many colleagues, both physicists and chemists, of the Physical Laboratory of the N. V. Philips' Gloeilampenfabrieken. I wish particularly to express my gratitude to the director, Professor G. Holst, to whom I am indebted for many valuable suggestions. Even more stimulating than his concrete suggestions were the many conversations which I had with him about the problems connected with this book.

Among my friends and coworkers I wish to thank chiefly Dr J. F. H. Custers, Dr C. J. Dippel, Dr W. Ch. van Geel, Dr M. C. Teves and Dr C. F. Veenemans. The results of many of the experiments carried out by us in common have been drawn upon in this book.

I am indebted to my friends Dr P. Clausing and Dr W. de Groot for many valuable suggestions, and especially to the former for permission to use many of the results of his unpublished work on oxide-coated cathodes (Chap. XIV).

My sincere thanks are due to Mrs H. E. Teves-Acly for her translation of the Netherlands manuscript. The work done by her and her husband, Dr M. C. Teves, on behalf of this book has been of the greatest value.

J. H. DE B.

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## CHAPTER I

### ELECTRON EMISSION FROM METALS

#### § 1. The electrons in a metal.

A metal consists of positive ions and electrons. The positive ions are arranged in a three-dimensional pattern, giving a periodic potential function in three dimensions. A group of the electrons is more or less free, that is, these electrons are not bound permanently to atomic systems, but may wander in the periodic potential field of the atom-ions (conduction electrons).

In the classical theory it was assumed that the electrons in the metal followed the Maxwellian distribution, so that at absolute zero their energy was zero, and at a temperature  $T$  the average thermal energy of a single electron was  $\frac{3}{2}kT$ , where  $k$  is the Boltzmann constant. The electrical and thermal conductivity of metals can be explained by the use of this theory, but a difficulty arises in the case of the specific heat, where it becomes necessary to assume that electron energy is independent of temperature, and that the electrons in a metal do not contribute to its specific heat.\*

In the modern metal theory electrons follow the distribution of Fermi-Dirac instead of that of Maxwell. At absolute zero the electron energy is not zero, but the energies of the electrons range from zero up to a maximum value  $W_i$ , the average energy of an electron being  $\frac{3}{8}W_i$ . The electrical and thermal conductivities, as well as the specific heat and optical properties of metals, can be satisfactorily explained by the use of this theory. For some of these properties the influence of the positive ions must be taken into account.

Electrons can be liberated from metals in several ways,

\* Cf. W. Wien, *Vorlesungen über neuere Probleme der theoretischen Physik*, p. 31, Teubner, Leipzig and Berlin (1913); W. Keesom in *Vorträge über die kinetische Theorie der Materie und der Elektrizität*, p. 194, gehalten in Göttingen, Teubner, Leipzig and Berlin (1914).



when a sufficient amount of energy is provided. Thus emission is possible:

- (1) By heating—thermionic emission.
- (2) By causing absorption of visible or ultraviolet light rays—photoelectric emission.
- (3) By applying very intense electric fields—auto-electronic emission (cold-cathode effect, field currents).
- (4) By bombarding with electrons—secondary electron emission.
- (5) By bombarding with metastable atoms or positive ions.

This book will deal with thermionic and photoelectric emission as modified by adsorption phenomena, and with the converse, the adsorption phenomena as they may be studied from the emission of electrons. In the following sections, therefore, a short review will first be given of the main features of thermionic and photoelectric emission phenomena in the case of pure metals. For more detailed information, readers are advised to refer to the following books or articles which have appeared within the last few years:

#### *Thermionic emission*

- W. Schottky and H. Rothe, Wien-Harms' *Handbuch der Experimentalphysik*, **13**, 2 (1928).  
S. Dushman, *Rev. Mod. Phys.* **2**, 382–476 (1930).  
A. L. Reimann, *Thermionic Emission*, Chapman and Hall, London (1934).

#### *Photoelectric emission*

- A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, McGraw Hill Book Co. Inc., New York and London (1932).  
B. Linford, *Rev. Mod. Phys.* **5**, 34–61 (1933).  
R. Suhrmann, *Ergebnisse der exakten Naturwissenschaften*, Berlin, **13**, 148 (1934).

#### *Various types of emission*

- K. T. Compton and I. Langmuir, *Rev. Mod. Phys.* **2**, 123–243 (1930).

*Application of modern theory*

K. K. Darrow, *Rev. Mod. Phys.* **1**, 90–157 (1929).

L. Nordheim, *Phys. Z.* **30**, 177–97 (1929).

A. Sommerfeld and H. Bethe, Geiger-Scheel's *Handbuch der Physik*, **24**, 2 (1934).

## § 2. Thermionic emission in classical theories.

It has been known for two hundred years that a metal, heated to a high temperature in air, loses positive or negative electricity, but it was only after the fundamental researches of Richardson\* that an exact knowledge of thermionic electron emission was gained.

When a metal filament, heated *in vacuo*, is made electrically negative (cathode) with respect to another metal filament or plate (anode), an electric current flows. Electrons are liberated from the heated metal cathode and flow toward the anode. They leave the metal with a definite kinetic energy depending upon the temperature of the cathode, so that even at positive potentials of the "cathode" which are not too high with respect to the anode, the electron current flows. If the cathode is made more and more negative, the current rises to a maximum value, the saturation current (see, however, § 9). The value of the saturation current depends only upon the temperature of the cathode and the metal used.

From the classical theory of metallic conduction Richardson† derived his well-known equation for emission:

$$i = aT^{\frac{1}{2}} e^{-\frac{b}{T}},$$

where  $i$  stands for the saturation current per unit area of the emitting metal,  $T$  the absolute temperature of that metal,  $e$  the base of the natural logarithmic system, and  $a$  and  $b$  are constants characteristic of the emitting surface. Subsequently,

\* O. W. Richardson, *Proc. Camb. phil. Soc.* **11**, 286 (1901); *Philos. Trans. A*, **201**, 497 (1903).

† Cf. O. W. Richardson, *The Emission of Electricity from Hot Bodies*, Longmans, Green and Co. (1921).

Richardson and v. Laue\* pointed out that the equation

$$i = AT^2 e^{-\frac{b_0}{T}} \quad \dots\dots(1)$$

could be derived, which is also in satisfactory agreement with observed data. In this equation  $b_0$  is a measure of the energy necessary to get the electron out of the metal.  $A$  is a universal constant, the value of which was derived by Dushman† by treating the problem of electron emission in the same way as the evaporation of a monatomic gas is treated in thermodynamics. The relation between the heat of sublimation per mol,  $L$ , and the vapour pressure,  $p$ , is given by the well-known formula of Clausius-Clapeyron:

$$L = RT^2 \left( \frac{d \log p}{dT} \right),$$

or in an integrated form:

$$\log p = \frac{1}{R} \int \frac{LdT}{T^2} + \text{const.},$$

where const. is the integration constant, and  $R$  is the molar gas constant = 1.987 cal./deg.

$L$  is a function of the temperature and can be expressed by the following relation:

$$L = L_0 + \int_0^T C_p dT - \int_0^T c_p dT,$$

where  $C_p$  denotes the specific heat of the vapour at constant pressure, and  $c_p$  that of the solid. Now considering the metal in equilibrium with an electron atmosphere, which is so dilute that mutual repulsions may be neglected, the electron atmosphere outside the metal will have the same specific heat as the molecules of a monatomic gas

$$C_p = \frac{5}{2} R.$$

As we have seen in § 1 the electrons in the metal are assumed not to contribute to the specific heat of the metal, so

$$c_p = 0$$

and

$$L = L_0 + \frac{5}{2} R.$$

\* O. W. Richardson, *Phil. Mag.* **28**, 633 (1914); M. v. Laue, *Jb. Radioakt.* **15**, 205, 207 (1918); compare also foot-note \* on p. 1.

† S. Dushman, *Phys. Rev.* **21**, 623 (1923).

When we substitute this in the equation for  $\log p$ , we get

$$\log p = -\frac{L_0}{RT} + \frac{5}{2} \log T + \text{const.},$$

where const. is the integration constant. According to Sackur\*

$$\text{const.} = K + \frac{3}{2} \log M,$$

where  $K$  is a universal constant, and  $M$  the molecular weight of the gas. In our case  $M = Nm$  ( $m$  = mass of an electron,  $9.02 \times 10^{-28}$  g.;  $N$  = Avogadro's number,  $6.06 \times 10^{23}$ ), so

$$p = N^{\frac{3}{2}} m^{\frac{3}{2}} e^K T^{\frac{5}{2}} e^{-\frac{L_0}{RT}}.$$

The number of electrons  $n$ , striking the metal surface per unit area in unit time, is given in the kinetic theory of gases by the relation

$$n = \frac{p}{\sqrt{2\pi m k T}},$$

where  $k$  = Boltzmann's constant,  $1.372 \times 10^{-16}$  erg/deg.

So the electron current is

$$i = n\epsilon = \left( \frac{N^{\frac{3}{2}} m \epsilon e^K}{\sqrt{2\pi k}} \right) T^{\frac{5}{2}} e^{-\frac{L_0}{RT}},$$

where  $\epsilon$  denotes the charge of a single electron. The chemical constant  $K$  is given by the relation†

$$K = \log \left[ \frac{(2\pi)^{\frac{3}{2}} k^{\frac{5}{2}}}{N^{\frac{3}{2}} h^3} \right].$$

So

$$i = \left( \frac{2\pi k^2 m \epsilon}{h^3} \right) T^{\frac{5}{2}} e^{-\frac{L_0}{RT}},$$

where  $h$  is Planck's constant,  $6.55 \times 10^{-27}$  erg-sec.

Denoting  $\frac{2\pi k^2 m \epsilon}{h^3}$  by  $A$ , and  $\frac{L_0}{R}$  by  $b_0$ , we get

$$i = A T^{\frac{5}{2}} e^{-\frac{b_0}{T}},$$

$A = 1.80 \times 10^{11}$  e.s.u./cm.<sup>2</sup> deg.<sup>2</sup> = 60.2 amp./cm.<sup>2</sup> deg.<sup>2</sup> The so-called thermionic work function  $\phi_0$  at absolute zero (expressed

\* O. Sackur, *Ann. Phys., Lpz.*, **36**, 958 (1911); **40**, 67 (1913).

† O. Sackur, *loc. cit.*; H. Tetrode, *Ann. Phys., Lpz.*, **38**, 404 (1912).

in volts) is related to  $L_0$  by the following equation:

$$\phi_0 = \frac{L_0}{N\epsilon} = \frac{Rb_0}{N\epsilon} = \frac{kb_0}{\epsilon} = 8.62 \times 10^{-5} b_0 \text{ volt.}$$

### § 3. Electron emission in modern theory.

In the atom an electron has three quantum numbers which, according to Bohr's theory, define its orbit, and a fourth quantum number which determines its spin about its own axis. This spin quantum number has only two possible values,  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . By the exclusion principle of Pauli all the electrons in an atom must differ from each other by at least one of their quantum numbers. Each orbit can, therefore, contain but two electrons, since there are only two possible values of the spin quantum number for each orbit.

The exclusion principle of Pauli led Fermi and Dirac to formulate a new distribution law which differs in the case of metals from that of Maxwell, and is called the "Fermi-Dirac statistics". From the Fermi-Dirac statistics, Pauli, and especially Sommerfeld\*, arrived at a new electron theory of metals. According to this theory all the valence electrons in the metal have a definite energy at  $0^\circ \text{K.}$ , which varies for different electrons from zero to a value  $W_i$ , and which can be calculated from the formula

$$W_i = \frac{h^2}{8m} \left( \frac{3n}{\pi} \right)^{\frac{2}{3}},$$

where  $h$  is Planck's constant,  $m$  is the mass of an electron, and  $n$  is the number of free electrons per unit volume of the metal. The value of  $W_i$ , the energy of the fastest electrons in the metal at  $0^\circ \text{K.}$ , ranges for the different metals from about 2 electron volts for the alkali metals to about 10 electron volts for the heavy metals. For potassium the value is 2.1 electron volts, and for tungsten 5.7 electron volts, assuming one free electron per atom.

The distribution function of the velocity of electrons in the metal is given by

$$f(\xi, \eta, \zeta) d\xi d\eta d\zeta = \frac{2m^3}{h^3} \frac{d\xi d\eta d\zeta}{e^{\frac{1}{2}m(\xi^2 + \eta^2 + \zeta^2) - W_i} + 1},$$

\* A. Sommerfeld, *Z. Phys.* **47**, 1 (1928).

where  $f(\xi, \eta, \zeta) d\xi d\eta d\zeta$  is the number of electrons per unit volume, whose velocity components  $\xi$ ,  $\eta$  and  $\zeta$  in the three directions in space  $x$ ,  $y$  and  $z$  lie in the range  $d\xi$ ,  $d\eta$ ,  $d\zeta$ . At absolute zero this function is constant and equal to  $\frac{2m^3}{h^3}$  for all energies of the electrons less than  $W_i$ , or when

$$\frac{1}{2}mv^2 = \frac{1}{2}m(\xi^2 + \eta^2 + \zeta^2) < W_i,$$

and is zero for all energies of the electrons greater than  $W_i$  (Fig. 1, solid line).

For higher temperatures there is an exponential drop in the function where the energy is nearly equal to  $W_i$  (broken line in

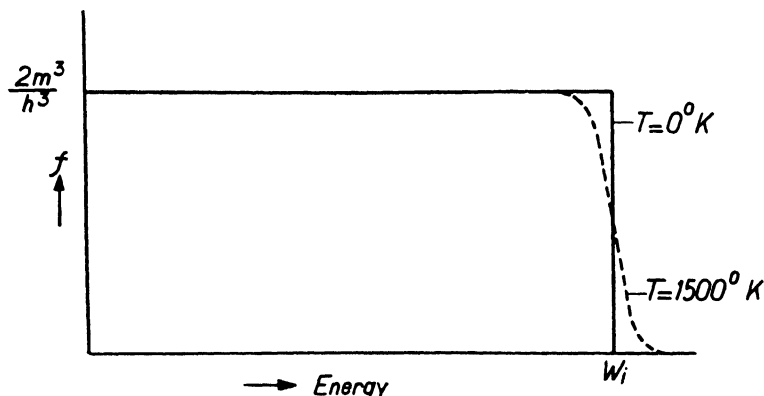


Fig. 1. Distribution function of the velocity of electrons in a metal.

Fig. 1). The function has half the value  $\frac{2m^3}{h^3}$  when  $\frac{1}{2}mv^2 = W_i$ .

Thus, according to the new theory, electrons have energies up to  $W_i$  at absolute zero, while at higher temperatures a few of the fastest electrons have energies above that value. In the classical theory the electrons were at rest, i.e. had zero energy, at absolute zero, and an increase of temperature increased the energy of all electrons.

Notwithstanding the high values of energy of some electrons at  $0^\circ\text{K}$ ., they remain within the metal, since the forces exerted by the positive ions and by the other free electrons prevent them from escaping.

When we denote by  $W_a$  the change in potential energy of a single electron after it has been removed from the metal,

$W_a$  is the work required to overcome the above-mentioned attractive forces, and corresponds to the energy required to remove an electron which is initially at rest in the metal. For removing electrons already possessing a kinetic energy  $W_i$  in the metal a smaller energy,  $W_a - W_i$ , is required.

Sommerfeld\* and Fowler and Nordheim† assumed that all those electrons which strike the surface of the metal with a velocity such that the component normal to the surface  $\xi$  is greater than a value  $\xi_0$  given by the relation

$$\frac{1}{2}m\xi_0^2 = W_a,$$

will leave the metal and contribute to the thermionic current. By letting  $\frac{1}{2}m\xi^2 = W$ , the normal energy, and  $N(W)dW$  be the number of electrons moving to the surface having normal energies between  $W$  and  $dW$ , Nordheim‡ deduced the relation

$$N(W) = \frac{4\pi m}{h^3} kT \log(1 + e^{-\frac{(W-W_i)}{kT}}).$$

When  $\frac{W_i - W}{kT} \gg 1$  and  $W < W_i$ :

$$N(W) = \frac{4\pi m}{h^3} (W_i - W),$$

when  $\frac{W - W_i}{kT} \cong 0$ :

$$N(W) \cong \frac{4\pi m}{h^3} kT,$$

and when  $\frac{W - W_i}{kT} \ll 1$  and  $W > W_i$ :

$$N(W) = \frac{4\pi m}{h^3} kT e^{-\frac{(W-W_i)}{kT}}.$$

At absolute zero the function of  $W$ ,  $(N(W))$ , is a straight line (solid line in Fig. 2). At higher temperatures  $N(W)$  decreases more gradually for the higher values of  $W$  (broken line in Fig. 2). By forming the integral of  $N(W)dW$  between the

\* A. Sommerfeld, *Z. Phys.* **47**, 1 (1928).

† R. H. Fowler, *Proc. roy. Soc. A*, **117**, 549 (1928); R. H. Fowler and L. Nordheim, *Proc. roy. Soc. A*, **119**, 173 (1928); R. H. Fowler, *Proc. roy. Soc. A*, **122**, 36 (1929).

‡ L. Nordheim, *Phys. Z.* **30**, 177 (1929).

limits  $W = W_a$  to  $W = \infty$ , the electron current per unit area can be expressed by the following:

$$i = 2 \frac{2\pi k^2 m \epsilon}{h^3} T^2 e^{-\frac{(W_a - W_i)}{kT}}.$$

This equation holds only for  $W_a - W_i \gg kT$ , which is usually the case.

Denoting as in § 2

$$\frac{2\pi k^2 m \epsilon}{h^3} \text{ by } A \text{ and } W_a - W_i \text{ by } kb_0,$$

we have

$$i = 2AT^2 e^{-\frac{b_0}{T}} \quad \dots\dots(2),$$

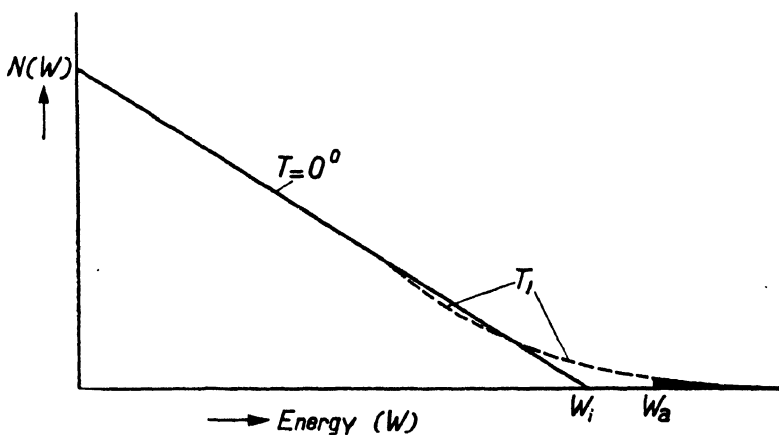


Fig. 2. Distribution function  $N(W)$  at absolute zero ( $T=0^\circ$ ) and at a higher temperature ( $T_1 > 0^\circ$ ).

an equation differing only by a factor 2 from the equation of § 2.

Since the thermionic work function  $\phi_0$  is equal to

$$\frac{W_a - W_i}{\epsilon},$$

$\epsilon$  being the absolute value of the charge of an electron,  $\epsilon\phi_0$  is the energy required to remove one of the electrons with the highest energy at absolute zero ( $W_i$ ) from the metal.

To some extent  $\epsilon\phi_0$  and  $W_a$  can be compared respectively to the ionization energy of an atom, and to the energy corresponding to the Röntgen K-absorption limit of the same atom, the ionization energy being the energy required to remove the



electron with highest energy in the atom, while the Röntgen K-absorption limit is a measure of the energy required to remove one of the most strongly bound electrons, the K electrons.\*

#### § 4. The value of $A$ in thermionics.

As has been shown in §§ 2 and 3, in the modern theory the thermionic current equation contains a factor  $2A$ , where in the Dushman theory  $A$  occurs. This difference comes from the fact that in every "cell" of the "phase space" two electrons can find a place having opposite spin moments. Most experiments are not sufficiently accurate to determine which value is the better, as the  $e$ -function dominates in the equation.

Nordheim† showed that not all the electrons in the metal, reaching the surface with a normal energy greater than  $W_a$ , will escape, but that, on the basis of wave mechanics, a certain number will be reflected back. The emission equation must therefore be multiplied by a factor  $(1 - R_e)$ , where  $R_e$  is the average reflectivity of the surface for electrons:

$$i = 2A (1 - R_e) T^2 e^{-\frac{b_0}{T}}$$

or, denoting  $2A (1 - R_e)$  by  $A_1$ ,

$$i = A_1 T^2 e^{-\frac{b_0}{T}} \quad \dots\dots(3).$$

The mean value of  $R_e$  depends on the temperature and on the value and slope of the potential distribution on both sides of the surface boundary. The discontinuous slope of potential Nordheim used led to a value  $R_e = \frac{1}{2}$ ; in this case  $A_1 = A$  again. If we accept a continuous slope the value of  $R_e$  will be about zero, so that

$$A_1 \sim 120 \text{ amp./cm.}^2 \text{ deg.}^2$$

It is known from experiment that the value of  $A_1$  depends to a great extent on the chemical purity of the surface. As will be shown later on, adsorption of electropositive elements decreases the value of  $A_1$ , whereas adsorption of electronegative elements increases the value. Experimentally found values

\* Of course, the comparison must not be carried too far. The conduction electrons in a metal are comparable to the valence electrons in an atom; the positive ions in a metal have of course K, L, etc. electrons of their own.

† L. Nordheim, *Z. Phys.* **46**, 833 (1927); *Proc. roy. Soc. A*, **121**, 626 (1928).

for  $A_1$  depend upon the state of the surface, and vary, for instance, for platinum\* from  $1.45 \times 10^7$  to  $10.7 \times 10^{-4}$ , and for hafnium† from 55,000 to 14.5. Measurements on pure metals, however, gave values for  $A_1$  in the neighbourhood of 100.‡ The following figures§ may be mentioned:

Molybdenum  $A_1 = 65$ ,

Tungsten  $A_1 = 100$ ,

Thorium  $A_1 = 70$ .

### § 5. Photoelectric emission.

The discovery of photoelectric emission from metals dates from experiments of Hertz|| in 1887, and Hallwachs¶ in 1888. In the following years Elster and Geitel\*\* published a series of studies of this phenomenon. They found a photoelectric effect in alkali metals and other metals for visible light, and constructed the first photoelectric cells. Lenard†† and J. J. Thomson‡‡ showed in 1899 that the electrically negative particles emitted under the influence of light were electrons.

Another discovery by Lenard was very important. He found that the kinetic energy, with which the electrons are released, is independent of the intensity of the light; the number of electrons, however, is proportional to this intensity. This was one of the basic facts upon which Einstein§§ built up his theory. According to Einstein light is absorbed as well as emitted in quanta of energy  $h\nu$ , where  $\nu$  is the frequency of light, and  $h$  is Planck's constant. This light energy is absorbed by electrons, and when we are dealing with a metal absorbing light, when  $\nu$  is great enough, the electrons of the metal will

\* Cf. L. A. DuBridge, *Phys. Rev.* **31**, 736 (1928).

† C. Zwikker, *Phys. Z.* **30**, 578 (1929).

‡ Cf. A. L. Reimann, *Nature*, Lond., **133**, 833 (1934).

§ C. Zwikker, *Proc. Roy. Acad. Amst.* **29**, 792 (1926).

|| H. Hertz, *Ann. Phys.*, Lpz., **31**, 983 (1887).

¶ W. Hallwachs, *Ann. Phys.*, Lpz., **33**, 301 (1888).

\*\* J. Elster and H. Geitel, *Ann. Phys.*, Lpz., **38**, 40, 497 (1889); **41**, 161 (1890); **42**, 564 (1891); **48**, 338, 625 (1892); **52**, 433 (1894); **55**, 684 (1895).

†† P. Lenard, *S.-B. Akad. Wiss. Wien*, **108**, 1649 (1899); *Ann. Phys.*, Lpz., **2**, 359 (1900).

‡‡ J. J. Thomson, *Phil. Mag.* **48**, 547 (1899).

§§ A. Einstein, *Ann. Phys.*, Lpz., **17**, 132 (1905).

absorb as much energy as is necessary to escape from the metal. Their maximum kinetic energy is then given by the relation:

$$\frac{1}{2}mv^2 = h\nu - W_P \quad \text{.....(4),}$$

where  $W_P$  is the work which must be done to liberate an electron from the metal.

This equation of Einstein has been very satisfactorily verified in later years. The energy of the emitted electrons can be determined by measuring the potential  $V_s$ , required to stop them:

$$V_s e = \frac{1}{2}mv^2 \quad \text{.....(5),}$$

$e$  being the charge of an electron. The frequency  $\nu_0$ , just capable of causing the emission of an electron with zero velocity, is given by

$$h\nu_0 = W_P.$$

$\nu_0$  is called the threshold frequency, the corresponding wavelength  $\lambda_0$  is called the long wave-length limit. The equation of Einstein can now be written

$$\frac{1}{2}mv^2 = h(\nu - \nu_0).$$

In modern metal theory those electrons whose normal energies,  $W$ , increased by the absorption of the energy quantum of light,  $h\nu$ , are increased to values greater than  $W_a$ , contribute to the photoelectric emission. When  $W + h\nu$  is equal to  $W_a$ , they escape with zero velocity; in general the kinetic energy of the emitted electrons will be

$$\frac{1}{2}mv^2 = W + h\nu - W_a.$$

As at absolute zero, maximum kinetic energy of the electrons in the metal is given by  $W_i$ , maximum kinetic energy of emitted electrons is given by

$$\frac{1}{2}mv_{\text{max}}^2 = h\nu + W_i - W_a.$$

So we see that

$$h\nu_0 = W_a - W_i.$$

According to § 3, the thermionic work function  $\phi_0$  is related to  $W_a - W_i$  by the equation

$$e\phi_0 = W_a - W_i.$$

So

$$h\nu_0 = e\phi_0.$$

The energy corresponding to the threshold frequency at absolute zero is equal to the energy corresponding to the thermionic work function.

At room temperature, the number of electrons having a greater energy than  $W_i$  is so small that the above-mentioned equations retain their validity. So, for these low temperatures, we see that the modern metal theory gives a good picture of the experimentally known fact that the curve giving the photoelectric current as a function of the voltage cuts the potential axis (with retarding potentials) at a finite angle.

At high temperatures, however, a large number of electrons have energies above  $W_i$ , so that the maximum energy is less sharply defined. In this case electrons will be emitted by radiation of lower frequency than  $\nu_0$  (consequently at a longer wave-length than  $\lambda_0$ ).

Wentzel, Fröhlich, Tamm and Schubin, and Penney\* formulated theories based on modern metal theory giving the spectral distribution curves, that is to say, the photoelectric emission as a function of the frequency. For our purpose it is unnecessary to treat these theories here. Tamm and Schubin treat the emission of electrons from the surface and from within the metal, i.e. the liberation of electrons from the field of the potential barrier at the surface and from the stronger fields of the crystal lattice. These latter electrons give a second threshold frequency  $\nu_0'$ . So the spectral distribution curve can be predicted to leave the axis at  $\nu = \nu_0$  with finite slope, then to pass a maximum with increasing frequency, and after a minimum to increase once more. For most metals this second threshold is far in the ultraviolet, where no measurements have been made. For potassium, however, the predicted curve of Tamm and Schubin is in good agreement with the experimentally known curve, measured by Suhrmann and Theissing.†

\* For a short treatment of these theories compare the book of Hughes and DuBridge and the article of Linford, mentioned in § 1; the theories themselves are published in: G. Wentzel, "Probleme der Modernen Physik", Sommerfeld *Festschrift*, p. 79 (1928); H. Fröhlich, *Ann. Phys.*, Lpz., **7**, 103 (1930); I. Tamm and S. Schubin, *Z. Phys.* **68**, 97 (1931); W. G. Penney, *Proc. roy. Soc.* **133**, 407 (1931).

† R. Suhrmann and H. Theissing, *Z. Phys.* **52**, 453 (1928).

### § 6. Effect of temperature on photoelectric emission.

As has already been pointed out in the foregoing section, the spectral distribution curve of photoelectrons cannot give at higher temperatures a finite point of intersection on the frequency (or wave-length) axis. Electrons, escaping at wave-lengths longer than  $\lambda_0$ , cause the curve to approach the axis asymptotically. Fowler\* calculated the number of electrons with such a component of velocity perpendicular to the surface that, after having taken up a quantity of light energy  $h\nu$ , they are able to escape from the metal. This number of electrons  $N_\epsilon$  can be expressed by the following equations:

$$\text{If} \quad \Delta = \frac{h(\nu - \nu_0)}{kT},$$

then for  $\Delta \leq 0$

$$N_\epsilon = \frac{2\sqrt{2}\pi m^{\frac{3}{2}}}{h^3} \frac{k^2 T^2}{(W_a - h\nu)^{\frac{1}{2}}} \left[ e^\Delta - \frac{e^{2\Delta}}{2^2} + \frac{e^{3\Delta}}{3^2} - \dots \right],$$

and for  $\Delta \geq 0$

$$N_\epsilon = \frac{2\sqrt{2}\pi m^{\frac{3}{2}}}{h^3} \frac{k^2 T^2}{(W_a - h\nu)^{\frac{1}{2}}} \left[ \frac{\pi^2}{6} + \frac{1}{2}\Delta^2 - \left\{ e^{-\Delta} - \frac{e^{-2\Delta}}{2^2} + \frac{e^{-3\Delta}}{3^2} - \dots \right\} \right].$$

From these equations we see that, for  $T \rightarrow 0$  and

$$\Delta \leq 0 \quad (h\nu \leq h\nu_0),$$

$$N_\epsilon = 0,$$

but when

$$\Delta \geq 0 \quad (h\nu \geq h\nu_0),$$

$$N_\epsilon \sim \frac{(h\nu - h\nu_0)^2}{(W_a - h\nu)^{\frac{1}{2}}}.$$

Further, we see that for  $\nu = \nu_0$

$$N_\epsilon \sim T^2.$$

Now the photoelectric current  $i$  may be assumed to be proportional to  $N_\epsilon$ , and

$$\frac{i(W_a - h\nu)^{\frac{1}{2}}}{T^2} = Cf(\Delta),$$

$f(\Delta)$  being used to denote the function in square brackets in the above equations, and  $C$  being a constant independent of  $\nu$  and  $T$ .

\* R. H. Fowler, *Phys. Rev.* **38**, 45 (1931).

When, in the experimental curves, the difference between  $\nu$  and  $\nu_0$  is not too great (not exceeding about 15 per cent.), then  $(W_a - h\nu)^{\frac{1}{2}}$  is nearly constant and equal to about  $W_{\frac{1}{2}}$ .

We can write the equations in the logarithmic form

$$\log \frac{i}{T^2} = B + \log f\left(\frac{h\nu - h\nu_0}{kT}\right) \quad \dots\dots(6),$$

where 
$$\log f\left(\frac{h\nu - h\nu_0}{kT}\right) = \log f(\Delta),$$

and 
$$\log f(\Delta) = \log\left(e^{\Delta} - \frac{e^{2\Delta}}{2^2} + \frac{e^{3\Delta}}{3^2} - \dots\right) \text{ for } \Delta \leq 0,$$

and

$$\log f(\Delta) = \log\left(\frac{\pi^2}{6} + \frac{1}{2}\Delta^2 - \left[e^{-\Delta} - \frac{e^{-2\Delta}}{2^2} + \frac{e^{-3\Delta}}{3^2} - \dots\right]\right) \text{ for } \Delta \geq 0.$$

As we shall see in § 7, these equations have already given excellent results in determining values of  $\nu_0$ .

### § 7. The thermionic work function and photoelectric threshold.

The energy required for freeing the fastest electrons from the metal 
$$W_a - W_i = kb_0 = \epsilon\phi_0 = h\nu_0$$

can be determined in several ways.

I. By plotting the values found experimentally from thermionic measurements of  $\log \frac{i}{T^2}$  against  $\frac{1}{T}$ ,  $b_0$  can be determined.

According to the equations for thermionic emission (formulae (1) of § 2, (2) of § 3, (3) of § 4)

$$i = A_1 T^2 e^{-\frac{b_0}{T}},$$

$$\log \frac{i}{T^2} = \log A_1 - \frac{b_0}{2.303} T.$$

This is the equation of a straight line, the slope of which gives  $b_0$ .

In this way the work function has been determined for a large number of metals, some of which are given in Table I.

Table I

Metal	$\phi_0$ in volts
Ag*	4.08
Pt†	6.27
Mo‡§	4.41
W‡§	4.52
Ta†	4.07
Th§	3.35

According to Reimann||  $\phi_0$  depends on temperature. Due to the thermal expansion of the metal, the concentration of free internal electrons is decreased, thus giving an increase of  $\phi_0$ . When  $A_1 = 120$  (§ 4), the following values are found for tungsten:

At 1600° K.: 4.65 volts,

At 2000° K.: 4.68 volts,

At 2500° K.: 4.72 volts.

II. The photoelectric threshold can be determined by the so-called *stopping potential method*. This method is based upon the Einstein equation (equations (4) and (5) in § 5)

$$\frac{1}{2}mv^2 = V_s e = h(\nu - \nu_0).$$

The stopping potentials are determined as a function of the frequency  $\nu$ . When different metals are used for anode and cathode, correction must be made for the contact difference of potential (§ 10). By plotting the stopping potentials as a function of  $\nu$ , a straight line is obtained, intercepting the frequency axis at  $\nu_0$ . This method, however, is more frequently used for determining Planck's constant  $h$  than for determining values of  $\nu_0$ .¶

III. The method commonly used for determining  $\nu_0$  is that of *spectral distribution curves*. In common practice the photoelectric current (based on unit intensity of light or not, eventu-

\* A. Goetz, *Z. Phys.* **43**, 531 (1927).

† L. A. DuBridge, *Phys. Rev.* **31**, 236; **32**, 961 (1928).

‡ S. Dushman, Rowe, Ewald and Kidner, *Phys. Rev.* **25**, 338 (1925).

§ C. Zwikker, *Proc. Roy. Acad. Amst.* **29**, 792 (1926).

|| A. L. Reimann, *Phys. Rev.* **45**, 898 (1934); *Nature*, Lond., **133**, 833 (1934).

¶ R. A. Millikan, *Phys. Rev.* **7**, 355 (1916); P. Lukirsky and S. Prilezaev, *Z. Phys.* **49**, 236 (1928).

ally reduced to a number of electrons per absorbed quantum) is plotted against wave-length. The interception with the wave-length axis gives  $\lambda_0$ , the long-wave limit.

IV. Another method for determining  $\nu_0$  is that which makes use of the complete photoelectric emission. When a metal surface is exposed to the total thermal radiation from a black body at a temperature  $T$ , the total photoelectric current is given by

$$i = A' T^2 e^{-\frac{h\nu_0}{kT}},$$

where  $\nu_0$  is the threshold frequency of the illuminated surface, and  $A'$  is a constant. This equation was given by Richardson,\* and later Suhrmann† and Roy‡ used it for determining  $\nu_0$ .

The lines obtained by plotting  $\log \frac{i}{T^2}$  against  $\frac{1}{T}$  are straight, and give work functions in good agreement with other methods. This method is very useful for studying variations of  $\nu_0$  with temperature, as the cathode temperature can be varied independently of the temperature of the black body.§

V. From the *equation of Fowler* (§6), giving the relation between temperature and photoelectric emission,  $\nu_0$  can be determined in the following manner. When  $\log f(\Delta)$  is plotted as a function of  $\Delta$  (equation (6) in §6), a universal curve is obtained.  $\log \frac{i}{T^2}$  from experimental data is plotted against  $\frac{h\nu}{kT}$ . A curve is obtained of the same shape as the universal curve, which can be made to coincide with it by a parallel shift. The vertical shift is a measure of  $B$ , the horizontal shift being equal to  $\frac{h\nu_0}{kT}$ . Thus  $\nu_0$  is determined here from the spectral distribution at a given temperature.

Instead of this *isothermic method*, DuBridge|| showed that good results can also be obtained from measurements at one

\* O. W. Richardson, *Phil. Mag.* **23**, 615 (1912); **24**, 570 (1912); **27**, 476 (1914).

† R. Suhrmann, *Z. Phys.* **33**, 63 (1925); **54**, 99 (1928).

‡ S. C. Roy, *Proc. roy. Soc. A*, **112**, 599 (1926); *Phil. Mag.* **50**, 250 (1925).

§ R. Suhrmann and H. Theissing, *Z. Phys.* **73**, 709 (1932).

|| L. A. DuBridge, *Phys. Rev.* **39**, 108 (1932).



frequency  $\nu$  but different temperatures (*isochromatic method*). For this purpose  $\log f(\Delta)$  is plotted against  $\log |\Delta|$ , and again a universal curve is obtained. From experimental data  $\log \frac{i}{T^2}$  is plotted against  $\log \frac{1}{T} = -\log T$ . Since

$$\log |\Delta| = \log \frac{|\hbar\nu - \hbar\nu_0|}{k} - \log T$$

the horizontal shift is now equal to

$$\log \frac{|\hbar\nu - \hbar\nu_0|}{k}.$$

Using the isothermic method DuBridge and Roehr\* found for extremely outgassed palladium as a mean value of measurements at eight different temperatures, varying from 305 to 1078° K.,

$$\phi_0 = 4.97 \pm 0.01 \text{ volts.}$$

Using the isochromatic method DuBridge found for the same palladium as a mean value of measurements at six different wave-lengths

$$\phi_0 = 4.96 \pm 0.02 \text{ volts.}$$

By means of the thermionic emission they found

$$\phi_0 = 4.99 \pm 0.04 \text{ volts,}$$

whereas the normal method by use of the spectral distribution curve gave

$$\phi_0 = 4.97 \text{ volts.}$$

## § 8. The nature of the work function.

One may now ask, what is the nature of the forces which prevent the electrons in the metal from escaping? In the first place, there are some electrons escaping and forming an electron atmosphere outside the metal. Due to the electric charges this electron atmosphere will have a great density in the direct neighbourhood of the surface, and will form an electrical double layer. When this electrical double layer is at equilibrium it prevents more electrons from escaping. It can be shown† that the fall of potential in this double layer must be

\* L. A. DuBridge and W. W. Roehr, *Phys. Rev.* **39**, 99 (1932).

† J. Frenkel, *Z. Phys.* **51**, 232 (1928); I. Tamm and D. Blochinzew, *Z. Phys.* **77**, 774 (1932).

equal to  $\frac{W_i}{\epsilon}$ . Outside the metal the electron density is very small and electrons there obey the Maxwell distribution, so that at absolute zero their energy can be assumed to be zero. Within the metal, however, energies up to  $W_i$  are present. Equilibrium will be reached when the potential fall of the double layer corresponds to maximum energy  $W_i$  in the metal.

Besides the forces of the double layer, there is another force which tends to draw an escaping electron back into the metal. An electron leaving the metal will polarize it. At a greater distance  $x$  from the metal, the force due to this polarization can be described as the electrostatic force between a positive charge within the metal, at a distance  $-x$  from the surface, and the electron (Fig. 3). The image force is thus equal to

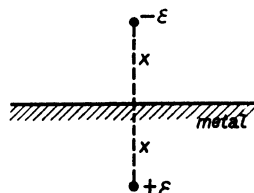


Fig. 3. An electron at a distance  $x$  from the metal is attracted as if there were an image of positive charge at a distance  $-x$  from the surface.

$$F = \frac{\epsilon^2}{(2x)^2}.$$

According to this image force, the energy required to remove an electron from a point at a distance  $r$  to infinity is equal to

$$Q = \int_r^\infty \frac{-\epsilon^2}{4x^2} dx = \frac{\epsilon^2}{4r}.$$

Due to these forces the energy value  $W_a$  is greater than  $W_i$ , as the difference  $W_a - W_i = \epsilon\phi_0$  must be ascribed to the action of this image force. Of course at distances smaller than about  $10^{-7}$  cm. the potential cannot be described by the above-mentioned equation, because it becomes necessary to take into account the influence of individual atoms. Schottky\* proposed to overcome this difficulty by considering the force an image force even in this region. Using this equation, however, up to infinitesimal distances from the surface, the calculated energy would become infinite. For this reason Schottky assumes the image forces to work up to a critical distance  $r_0$ ,

\* W. Schottky, *Z. Phys.* **14**, 63 (1923).

which was already used by Debye,\* and is so defined that at the distance  $r_0$  the tangent to the potential curve will cut the axis in the zero point (compare Fig. 4). From  $r_0$  the potential is assumed to decrease linearly with decreasing distance. The energy will then be equal to the sum of two parts, one, from the region infinity to  $r_0$ , being equal to  $\frac{\epsilon^2}{4r_0}$ , the other, from the region close to the metal, also being equal to  $\frac{\epsilon^2}{4r_0}$ , since in this region the force  $\frac{\epsilon^2}{4r_0^2}$  is constant.

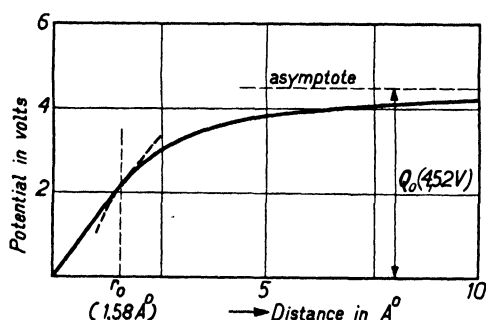


Fig. 4. Course of potential outside a metal, according to Schottky (the values relate to tungsten).

Expressed in volts, the work function will then be equal to

$$\phi_0 = \frac{300\epsilon}{2r_0} \text{ volts.}$$

$r_0$  proves to be of the magnitude of the distance between the atoms of the metal concerned. According to this correlation, metals having a great distance between the atoms, i.e. having a large atomic volume, have a small value of  $\phi_0$ , metals of high density a large value of  $\phi_0$ .† The alkali metals have, indeed, the lowest values of photoelectric threshold frequency and thermionic work function; metals such as platinum, tungsten, etc., have high values.

When a metal can exhibit several crystal modifications, one

\* P. Debye, *Ann. Phys.*, Lpz., **33**, 441 (1910).

† Foot-note added to proof: This correlation is treated in detail by F. Rother and H. Bomke, *Z. Phys.* **86**, 231 (1933); **87**, 806 (1934) H. Bomke, *Z. Phys.* **90**, 542 (1934); **91**, 400 (1934).

would expect that at the transition point there would also be a sudden jump in the value of the work function. The work function is actually higher for the phase of higher density and therefore smaller atomic separation.

In this connection Goetz\* showed by a careful study that the photoelectric threshold of the commonly known tetragonal modification of  $\beta$ -tin is found at  $2740 \pm 10 \text{ \AA}$ . ( $\phi_0 = 4.51$  volts), whereas the hexagonal  $\gamma$ -modification (above about  $200^\circ \text{ C.}$ ), having a greater atomic volume, shows  $\lambda_0 = 2820 \pm 10 \text{ \AA}$ . ( $\phi_0 = 4.38$  volts). Similarly for cobalt Cardwell† found  $\phi_0$  for the hexagonal closely packed modification to be  $4.25 \pm 0.08$  volts, whereas above  $850^\circ \text{ C.}$  cobalt gives a transition into a face-centred cubic lattice, having a greater atomic volume and giving a value of  $\phi_0$  equal to  $4.12 \pm 0.04$  volts.

There are some metals which show a contraction when passing into another modification, stable at higher temperatures. Thus the atomic volume of  $\gamma$ -iron (above  $910^\circ \text{ C.}$ ) is about 3 per cent. smaller than that of  $\alpha$ -iron.  $\gamma$ -iron seems also to have a smaller photoelectric sensitivity than  $\alpha$ -iron, so that it is possible that its  $\phi_0$  value is higher.

Investigations by Zwikker‡ have proved that zirconium and hafnium show a transition into another modification at higher temperatures, which was found by Burgers§ to be a transition from the hexagonal into a body-centred cubic one. Zwikker's measurements have already shown that the work function of hafnium has a greater value for the modification stable at high temperatures. The values are: ||

Hexagonal hafnium:  $\phi_0 = 3.20$  volts,

Regular hafnium:  $\phi_0 = 3.53$  volts.

And since Vogel and Tonn¶ found that in this case the transition to the modification stable at higher temperatures gives a

\* A. Goetz, *Phys. Rev.* **33**, 373 (1929).

† A. B. Cardwell, mentioned in the book of A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, pp. 65 and 105.

‡ C. Zwikker, *Physica*, **6**, 361 (1926).

§ W. G. Burgers, *Z. anorg. Chem.* **205**, 81 (1932).

|| Mentioned by J. H. de Boer and J. D. Fast, *Z. anorg. Chem.* **187**, 208 (1930).

¶ R. Vogel and W. Tonn, *Z. anorg. Chem.* **202**, 292 (1931).

contraction, here again the modification with the smallest atomic distance has the highest value of  $\phi_0$ .

Instead of the force function, proposed by Schottky (Fig. 5), Langmuir\* proposed the one given in Fig. 6. Its form is that of a parabola, rising from  $F(x)=0$  at the origin  $x=0$  to a maximum and then merging into the curve of the image force at  $x=r_0$ . Here again  $\phi_0 = \frac{300\epsilon}{2r_0}$  volts.

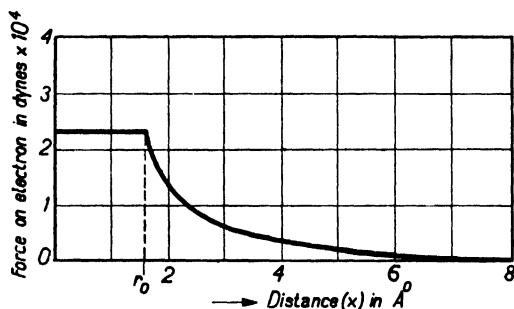


Fig. 5. Force on an electron, according to Schottky.

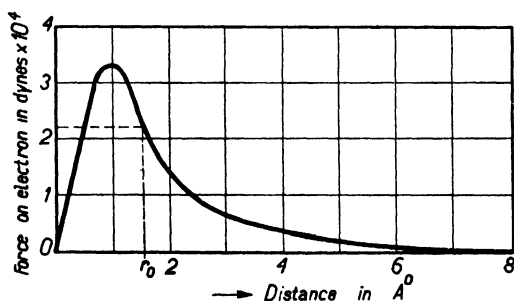


Fig. 6. Force on an electron, according to Langmuir.

According to the above-mentioned views, the picture of the total slope of potential can be given as in Fig. 7.

The magnitude of  $W_a$  plays a part in electron diffraction, as  $W_a$  will change the de Broglie wave-length

$$\lambda = \frac{h}{\sqrt{2m\epsilon V}},$$

\* I. Langmuir, *Trans. Amer. Electrochem. Soc.* **29**, 157 (1916).

when  $V$  is the accelerating potential for the beam of electrons, to

$$\lambda' = \frac{h}{\sqrt{2m\epsilon(V+W_a)}}.$$

Electron diffraction experiments of Davisson and Germer, Rupp and others\* give values for  $W_a$  as high as 14 electron volts for silver, 17 electron volts for aluminium, etc.

We are concerned with the energy required to extract an electron from the metal, but it is at the same time the energy we gain when an electron is given to the metal, since according to the Pauli exclusion principle, new electrons cannot be added on an energy niveau lower than  $W_i$ . The energy  $\epsilon\phi_0$  can thus be compared not only with the ionization energy of an atom, but also with the electron affinity of a halogen or an ox-

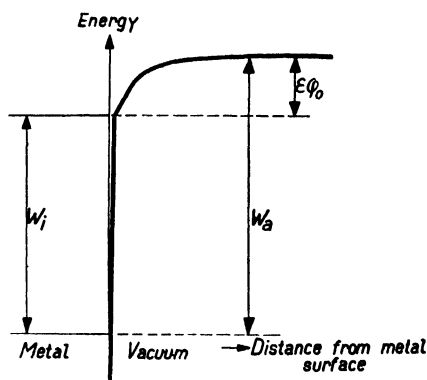


Fig. 7. Course of potential (energy) outside a metal.

## § 9. Electron emission in accelerating fields. Field currents.

If an electric field  $E_f$ , giving a constant force  $F_a = E_f e$ , is applied at the surface, the effective work function will be lowered (Fig. 8). It can easily be shown that†

$$r' = \frac{\epsilon}{2\sqrt{F_a}} = \frac{1}{2}\sqrt{\frac{\epsilon}{E_f}},$$

and

$$\phi' = \phi_0 - \sqrt{F_a},$$

where  $r'$  and  $\phi'$  denote respectively the distance and height of the maximum of the resulting curve given in Fig. 8. In this case

\* Cf. G. P. Thomson, *The Wave Mechanics of Free Electrons*, p. 99, McGraw Hill Book Co. Inc., New York and London (1930).

† W. Schottky and H. Rothe, *Handbuch der Experimentalphysik*, **13**, 2, p. 258 (1928).

the equation for thermionic emission becomes

$$i = A T^2 e^{\frac{-\epsilon(\phi_0 - \sqrt{F_a})}{kT}},$$

or

$$i = i_0 e^{\frac{\epsilon\sqrt{F_a}}{kT}},$$

when  $i_0$  is the current for zero external field. This shows why thermionic and also photoelectric currents never become completely saturated, but continue to increase with increasing fields. This Schottky effect has been verified for fields up to  $10^6$  volts/cm., where  $r' = 19 \times 10^{-8}$  cm.

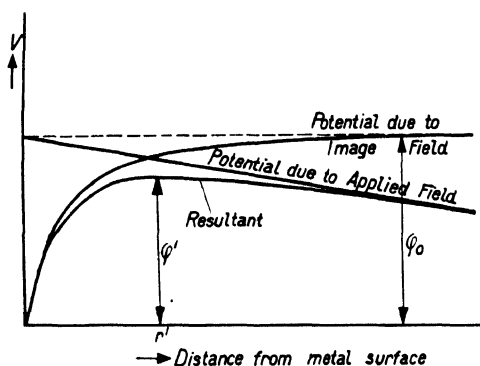


Fig. 8. Combination of the potentials due to applied field and due to image field.

At still higher fields the above-mentioned equation does not hold. By means of strong fields electrons can be extracted from metals even at room temperature. Measurements by Millikan and his collaborators\* and by others† agreed with the equation

$$i = A (T + cE_f)^2 e^{-\frac{b}{T + cE_f}},$$

where  $E_f$  is the field and  $c$  a constant. For strong fields and low temperatures the logarithm of the electron current is a linear function of the reciprocal of the field strength.

\* R. A. Millikan and C. F. Eyring, *Phys. Rev.* **27**, 51 (1926); C. F. Eyring, S. S. Mackeown and R. A. Millikan, *Phys. Rev.* **31**, 900 (1928); R. A. Millikan and C. C. Lauritsen, *Proc. Nat. Acad. Sci., Wash.*, **13**, 45 (1928); *Phys. Rev.* **33**, 598 (1929).

† Research staff of the General Electric Company, London, *Phil. Mag.* (7) **1**, 609 (1926).

On the basis of modern theory Fowler and Nordheim\* derived the equation

$$i = a E_f^2 e^{-\frac{b}{E_f}},$$

$a$  and  $b$  being constants for a given metal.

This electron emission in strong fields plays an important part in electrolysis, where neutralization of the ions at the electrodes is brought about by the extraction of an electron by the strong field of the ion itself. This phenomenon is also very important in photoelectric cells and dry rectifiers, and we shall meet it several times later in this book.

### § 10. Contact potential.

When two metals having different values of work function,  $\phi_{01}$  and  $\phi_{02}$ , are brought into contact, some electrons go from the metal with the smaller work function to that with the greater work function, leaving the first metal positive and making the second metal negative with respect to the other. We say then that the first metal is electropositive with respect to the second one.

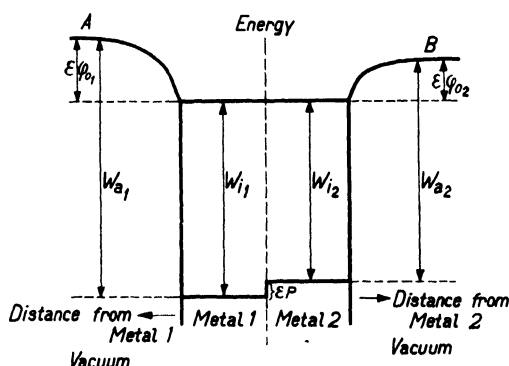


Fig. 9. Relative height of energy levels, when two metals are in contact with each other.

At the surface of contact a potential will result, which we may call the inner contact potential. Since at equilibrium the energies of electrons which can flow from one metal to another are the same, the height of the  $W_i$ -niveaus must be the same. From Fig. 9 we see that the inner contact potential  $P$ , which is

\* R. H. Fowler and L. Nordheim, *Proc. roy. Soc. A*, **119**, 173 (1928).



the difference in height between the electron energy niveaus of electrons with zero energy, will be given by  $\epsilon P = W_{i1} - W_{i2}$ .

The transfer of an electron from *A* to *B* (Fig. 10) at a first approximation requires no energy. Extraction of an electron from metal 1, however, requires the energy  $\epsilon\phi_{01}$  (Fig. 9); addition of an electron to metal 2 gives a gain  $\epsilon\phi_{02}$ , which has a smaller value than  $\epsilon\phi_{01}$ . As, however, metal 1 is negative with respect to metal 2, an electric double layer is formed, which gives an accelerating field. Therefore, this outer potential difference (Voltapotential), *V*, must be such that

$$\epsilon V = \epsilon\phi_{01} - \epsilon\phi_{02}$$

and

$$V = \phi_{01} - \phi_{02}.$$

In reality there is a small energy change (Peltier-effect) when an electron is transferred from one metal to another; this change being caused by the fact that the variation of  $W_i$  with temperature is not the same in both metals.

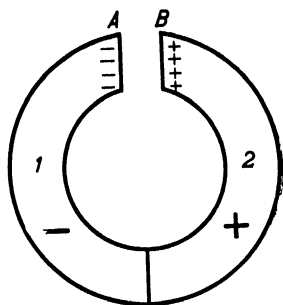


Fig. 10. When two metals make contact, one is positively charged with respect to the other.

## CHAPTER II

### THE NATURE OF ADSORPTION FORCES

#### § 11. Atoms and ions.

##### (a) *Constitution of an atom*

Atoms are built up of a positively charged nucleus and electrons. The number of electrons is such that the atom is neutral, and, moreover, the centre of gravity of the negative charges coincides with the positive nucleus. The electrons in an atom can be considered to be arranged in main groups: the *K*-group, the *L*-group, the *M*-group, the *N*-group, etc., and further in subgroups, all of which groups are defined by the so-called quantum numbers. The details of this arrangement would be out of place here; for our purpose it is only necessary to know that the groups are distinguished by the varying energy with which the electrons in the group are bound to the atom.

##### (b) *Ionization by absorption of light*

By the absorption of light an electron in an atom can be brought into a state in which it is less strongly bound to the remainder of the atom. The electron has thereby taken up an amount of potential energy, with respect to the remainder of the atom, which is given by the relation

$$\Delta Q = h\nu,$$

where  $\Delta Q$  denotes this amount of energy,  $\nu$  the frequency of the monochromatic light absorbed, and  $h$  Planck's constant (compare § 2). Since in free uncombined atoms the electron can exist only in certain states of energy with respect to the rest of the atom, which are governed by quantum rules, the atom cannot take up any arbitrary quantity of energy by light absorption, but only very definite quantities, which represent the difference in energy between one of those permitted "excited" states and the "normal" state. To these definite quantities of energy correspond certain, very definite, fre-

quencies  $\nu$ . The absorption spectrum of an atomic gas consists, therefore, of a definite number of absorption lines, which satisfy a distinct regularity. The absorption line with the longest wave-length, which corresponds to the smallest frequency and energy, is a measure of the smallest amount of energy with respect to the rest of the atom which the electron under consideration can take up by absorption of light. The frequency (or energy) separation of the absorption lines decreases in the direction of higher frequencies (shorter wave-lengths), and the lines converge toward a short wave-length limit, whose  $h\nu$  value represents the energy necessary entirely to remove the electron from the remainder of the atom, i.e. to ionize the atom. The short wave-length limit of the absorption spectrum gives us directly the *ionization energy* of the atom.

(c) *Ionization by other means*

A free atom can be ionized by other means than by the absorption of light, for example, by letting it collide with an electron possessing sufficient energy. In this method, which was originated by Franck and Hertz,\* electrons are allowed to pass through a definite potential difference  $V$ , and then to collide with the atom under consideration. If the energy of these electrons  $eV$  ( $e$  = charge of an electron) is equal to the ionization energy of the atom in question, the atom will be ionized. Here the ionization energy can be measured by the potential difference  $V$  through which the colliding electrons have to pass to obtain the energy necessary to cause ionization. One may thus speak of ionization potential, which is measured in volts. The *electron volt* (volts  $\times$  charge of an electron) can be used here as a unit of energy, where reference is usually to a gram molecule or a gram atom. If each of the atoms in one mol of a monatomic gas, i.e.  $6.06 \times 10^{23}$  atoms, gains the energy from one electron that has passed through a difference of potential of one volt ( $\frac{1}{3.10}$  e.s.u.), then the total gain in energy is  $6.06 \times 10^{23} \times \frac{1}{3.10} \times 4.77 \times 10^{-10} = 9.628 \times 10^{11}$  ergs

$$= 23.06 \text{ kg. cal.,}$$

so that one electron volt is equal to 23.06 kg. cal.

\* J. Franck and G. Hertz, *Ber. dtsh. phys. Ges.* **16**, 457 (1914).

(d) *Tendency to form ions with the electron structure of an inert gas*

Atoms, which in the periodic system immediately follow the inert gases, helium, neon, argon, krypton and xenon, can lose electrons with relative ease and become positive ions. Such elements are the alkali metals, lithium, sodium, potassium, rubidium and caesium, and the alkaline earth metals, beryllium, magnesium, calcium, strontium and barium. The electrons which these elements possess, beyond the number possessed by the preceding inert gas, belong to a new, less strongly bound group, and it is just these electrons which can easily be lost by ionization of the atom. The alkali metals form singly charged positive ions, and the alkaline earth metals may form doubly charged positive ions upon ionization, while elements like aluminium, yttrium and lanthanum may form positive ions with a triple charge, zirconium, hafnium and thorium positive ions with a quadruple charge, etc. All the positive ions thus formed have the electron structure of the preceding inert gas.

(e) *Ionization energies*

Table II gives the ionization energies of some of those elements mentioned in the preceding paragraph. From this table it can be seen that a large amount of energy is necessary to remove an electron from one of the inert gases, and that it is difficult to remove an electron from an ion which has taken on the electron structure of an inert gas. It must be noted in addition that the work of ionization in one and the same group becomes smaller as the atomic number of the element increases. So, for instance, less work is done in ionizing an atom of caesium than one of sodium or lithium, and less in ionizing an atom of barium than one of calcium or magnesium. Finally the work necessary to remove a second electron from a positive ion which already has a single charge is naturally much greater than that which was necessary to remove the first electron; it is nearly double the latter work when both electrons belong to the same group (see  $I_1$  and  $I_2$  for Be ... Ba).

Table II

Atomic number	Element	Work of ionization first electron $I_1$ in electron volts	Work of ionization second electron $I_2$ in electron volts	Work of ionization third electron $I_3$ in electron volts
2	He	24.47	—	—
10	Ne	21.47	—	—
18	A	15.68	—	—
36	Kr	13.94	—	—
54	Xe	12.08	—	—
86	Nt	10.69	—	—
3	Li	5.37	75.28	—
11	Na	5.12	47.5	—
19	K	4.32	31.7	—
37	Rb	4.16	27.3	—
55	Cs	3.88	23.4	—
4	Be	9.28	18.14	153.10
12	Mg	7.61	14.97	81
20	Ca	6.09	11.82	50.8
38	Sr	5.67	10.98	—
56	Ba	5.19	9.95	—

The atoms of the heavy metals lose electrons much less easily than those of the alkali and alkaline earth groups, i.e. the ionization energies of the heavy metals are greater. Table III gives a list of the ionization energies of some of these heavy metals.

Table III

Atomic number	Element	$I_1$ in electron volts	$I_2$ in electron volts
29	Cu	7.69	20.2
47	Ag	7.54	17.1
79	Au	9.19	—
80	Hg	10.39	18.67
78	Pt	8.9	—

(f) *Electron affinity*

The elements which precede the inert gases by one, two or more places in the periodic system have the tendency to take up enough electrons to give them the configuration of the following inert gas, and thereby form negative ions. The so

formed singly charged chlorine ion, for example, takes on the configuration of argon, the singly charged negative fluorine ion and the doubly charged negative oxygen ion both take on the configuration of neon.

Energy is gained by the addition of an electron to a halogen atom. This electron affinity,  $E$ , decreases in the halogen group from fluorine to iodine. The addition of one electron to an atom of oxygen results in a gain of energy, while work must be done to cause the addition of a second electron and thus the formation of a doubly charged oxygen ion.

Several values of electron affinity are given in Table IV.\*

Table IV

Element	$E$ , electron affinity in electron volts
F	4.1
Cl	3.75
Br	3.55
I	3.2
O	$-6.5 \pm 2$
S	$-4.0 \pm 2$

## § 12. Chemical combination.

### (a) *Combination of ions to molecules*

Many chemical compounds are built up of ions. The force which keeps the ions together is the Coulomb electrostatic attraction between the positive and negative charges on the ions. In the formation of a molecule of sodium chloride from a sodium atom and a chlorine atom the following quantities of energy take part: the energy of ionization of the sodium atom, the electron affinity of the chlorine atom, and finally the electrostatic attraction between the chlorine and sodium ions. This combination of ions is the basis of the famous theory of Kossel† dealing with chemical combination, first published in

\* For these values cf. A. E. van Arkel and J. H. de Boer, *Chemische Bindung*, Leipzig (1931); J. E. Mayer and L. Helmholz, *Z. Phys.* **75**, 19 (1932); J. E. Mayer and M. McC. Maltbie, *Z. Phys.* **75**, 748 (1932).

† W. Kossel, *Ann. Phys.*, Lpz., **49**, 229 (1916).

1916, and later by Kossel and others\* elaborated into a complete system.

(b) *Lattice energy*

If we start with solid sodium and molecular, gaseous chlorine, work must be done to vaporize the sodium and to dissociate the molecules of chlorine  $\text{Cl}_2$  into atoms, while energy is gained upon the formation of the solid sodium chloride by the condensation of the salt from its gaseous molecules. Since the solid crystalline form of the salt is also built up of ions, this latter energy can be calculated by means of Coulomb forces, by making a summation of the mutual energies between the ions. The *lattice energy*, i.e. the energy gained when a gram molecule of an ionic compound is condensed from its free gaseous ions, is, therefore, obtained by a summation of terms

$$\frac{\epsilon^2}{r},$$

where  $\epsilon$  is the charge of one ion (in this case a single charge, otherwise  $z\epsilon$ ), and  $r$  is the distance between two ions. This energy can therefore be expressed in the following form:

$$U = A_M \frac{\epsilon^2}{d},$$

in which  $A_M$  is the constant of summation (Madelung constant), and  $d$  is the shortest distance between two ions in the lattice. In the sodium chloride crystal  $A_M$  is equal to 1.747.

(c) *Repulsive forces*

Even though the ions in a chemical compound exert a mutual attraction, they cannot approach to within any arbitrary distance of each other. At a certain point repulsive forces begin to be effective, and increase rapidly with decreasing distance. Until recent years these repulsive forces were expressed by the following formula:

$$F = \frac{B}{r^n},$$

\* Cf. A. E. van Arkel and J. H. de Boer, *Chemische Binding*, Amsterdam, German edition translated by Li and W. Klemm, Leipzig (1931).

where  $n$  was considered to be about 10, and  $B$  was a constant. Better results are given by the expression proposed later by Born and Mayer:\*

$$F = be^{-\frac{r}{\rho}},$$

where  $b$  and  $\rho$  are constants,  $\rho$  having a value of  $0.345 \times 10^{-8}$  cm. at least for all alkali halides.

#### (d) Potential curves

As a result of this repulsive force the ions at equilibrium remain apart by a certain distance  $r_0$ , such that the repulsive and attractive forces are just equal. We can trace the "potential

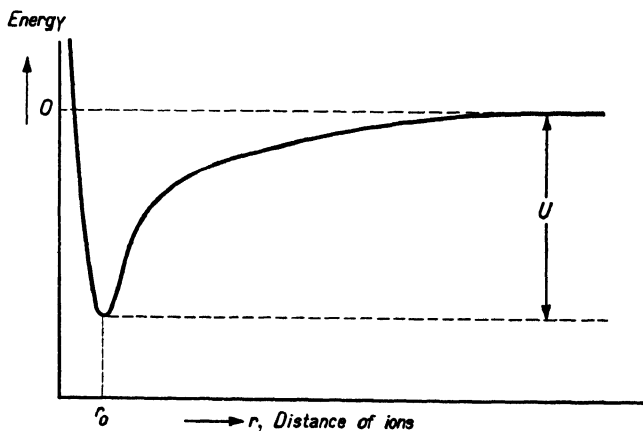


Fig. 11. Potential curve for an ionic compound. Energy as a function of distance of ions.

curve" (Fig. 11) by taking as abscissa the distance between the ions, and as ordinate the energy of the ionic system characteristic of the compound, and by letting the potential energy equal zero when the ions are infinitely far apart. From the above explanation it becomes plain that  $r_0$  in Fig. 11 is the separation of the ions at equilibrium, and that the length of the perpendicular from the minimum of the curve to the axis of zero energy represents the energy of combination, which, when reference is to a gram molecule of a solid salt, is equal to the lattice energy  $U$ .

\* M. Born and J. E. Mayer, *Z. Phys.* 75, 1 (1932).



(e) *Atomic compounds*

A chemical compound may be formed not only by the combining of *ions* but also by the combining of *atoms*.\* In the latter case the molecule is made up of neutral components, which possess electrons in common. The components are here again bound together by Coulomb attractive forces, in this case between the valence electrons and the remainders of the atoms (ions).

Such bonds exist in molecules which are made up of two similar atoms, for example,  $H_2$ ,  $Cl_2$ ,  $O_2$ , etc., and between the carbon atoms in organic compounds, and very probably between the carbon and hydrogen atoms in organic compounds. Between the bond in ionic compounds and that in atomic compounds all kinds of intermediate forms of bond are possible.

## § 13. Polarization, dipoles, and van der Waals' forces.

(a) *Polarization*

As has already been noted in § 11, the centre of gravity of the negative charges of an atom is coincident with that of the positive charges. The same is the case with ions.

Under the influence of an electric field, however, the negative charges can be shifted in position with respect to the positive, creating a so-called *electric dipole*, which is characterized by the dipole moment  $\mu$ , equal to the product of the shifted charge  $ze$  and the distance  $l$  through which the charge is moved,

$$\mu = ze l.$$

If the electric field is not chosen too great, the size of the induced dipole moment is proportional to the value of the field  $E_f$ ,

$$\mu = \alpha E_f.$$

The proportionality factor  $\alpha$  is called the polarization constant of the atom or ion under consideration, and has the dimensions of a volume. The polarization constants of many ions are fairly well known, those of atoms, however, are not so well known. Table V gives the values of  $\alpha$  for the alkali metal ions and atoms, which latter are very uncertain.

\* W. Heitler and F. London, *Z. Phys.* **44**, 455 (1927).

Table V

Ion*	$\alpha$	Atom	$\alpha^\dagger$	$\alpha^\ddagger$	$\alpha^\S$	$\alpha  $
Li <sup>+</sup>	$0.08 \times 10^{-24}$	Li	$27 \times 10^{-24}$	$32 \times 10^{-24}$	—	$12 \times 10^{-24}$
Na <sup>+</sup>	$0.20 \times 10^{-24}$	Na	$27 \times 10^{-24}$	$25 \times 10^{-24}$	—	—
K <sup>+</sup>	$0.88 \times 10^{-24}$	K	$46 \times 10^{-24}$	$42 \times 10^{-24}$	—	$34 \times 10^{-24}$
Rb <sup>+</sup>	$1.40 \times 10^{-24}$	Rb	$50 \times 10^{-24}$	$43 \times 10^{-24}$	—	—
Cs <sup>+</sup>	$2.46 \times 10^{-24}$	Cs	$61 \times 10^{-24}$	—	$46 \times 10^{-24}$	$42 \times 10^{-24}$

(b) *Energy related to polarization*

For the polarization of an atom or ion, whose polarizability is  $\alpha$ , and upon which a dipole moment  $\mu$  is induced, energy must be supplied to the value

$$\frac{\mu^2}{2\alpha}.$$

However, in an inhomogeneous electric field, such an induced dipole will be attracted to a point of lower potential, by which process energy is gained. When in the formation of chemical compounds or in adsorption processes ions polarize other ions or atoms, the energy freed by the above-mentioned attraction is twice the energy used to induce the dipole. The energy of combination  $Q_2$  of a dipole having a moment  $\mu$ , at a distance  $r$  from an ion with a charge  $\epsilon$ , is given by

$$Q_2 = \frac{\epsilon\mu}{r^2}.$$

If the dipole is first induced in an atom or ion with a polarizability  $\alpha$ , by the polarizing action of the given ion, the energy  $Q_1$  necessary for this is given by

$$Q_1 = \frac{\mu^2}{2\alpha},$$

where  $\mu$  is given by the relation

$$\mu = \alpha E_f = \alpha \frac{\epsilon}{r^2},$$

\* K. Fajans and G. Joos, *Z. Phys.* **23**, 1 (1924); M. Born and W. Heisenberg, *Z. Phys.* **23**, 388 (1924).

† E. Fues, *Z. Phys.* **82**, 536 (1933).

‡ K. F. Herzfeld, *Phys. Rev.* **29**, 701 (1927).

§ J. H. de Boer, *Chem. Weekblad*, **29**, 34 (1932).

|| H. Scheffers and J. Stark, *Phys. Z.* **35**, 628 (1934).

since the electric field of the ion is equal to  $\frac{\epsilon}{r^2}$  at a distance  $r$ .

The total energy gained by the process of polarization and the combination of the so-formed induced dipole is

$$Q = Q_2 - Q_1 = \frac{\epsilon\mu}{r^2} - \frac{\mu^2}{2\alpha} = \frac{\alpha\epsilon^2}{r^4} - \frac{\alpha^2\epsilon^2}{2\alpha r^4} = \frac{\alpha\epsilon^2}{2r^4}.$$

In the formation of a molecule by the combining of ions, the ions mutually polarize each other, whereby the energy of combination is increased.

### (c) *Molecules with a permanent dipole*

While *molecules* are electrically neutral, they are not necessarily electrically symmetrical, that is to say, the centre of gravity of the negative charges is not necessarily the same as that of the positive charge. Molecules may thus possess a *permanent electric moment*. Such a dipole molecule can enter into combination electrostatically with ions to form an addition product. This phenomenon occurs in the hydration of ions, and plays a very important part in the chemistry of complex compounds, and in surface chemistry. Some molecules with permanent electric dipoles are the following: water, ammonia, sulphur dioxide, methyl chloride, chloroform, alcohols, ethers, ketones, acids, amines, etc. In spite of the fact that the formulae of such molecules as water and sulphur dioxide can be written symmetrically, these molecules are not symmetrically constituted, because the polarizability of the central component is too great. On the other hand, other molecules whose formulae can be written symmetrically really have a symmetrical structure and possess no dipole moment; for example, carbon dioxide, methane, and all saturated hydrocarbons, carbon tetrachloride, benzene, etc.

### (d) *van der Waals' forces*

Two neutral atoms or molecules with no dipole may, in spite of the lack of charge or dipole, still exert attractive forces upon each other. These *universal cohesive forces*, or *van der Waals' forces*, arise from the fact that although an atom is electrically

symmetrical on the average over a length of time, it is asymmetrical during an infinitesimal moment, and can therefore exert a polarizing influence on another atom. The continually varying field induces in another atom a continually varying dipole, so that, although on the average over a length of time the whole remains electrically symmetrical, this interaction results in a permanent attraction between the atoms.

According to an approximation formula derived by London\* this van der Waals reciprocal energy between two atoms  $i$  and  $k$  can be represented by the formula

$$Q = \frac{3}{2} \cdot \frac{\alpha_i \alpha_k}{r^6} \cdot \frac{I_i I_k}{I_i + I_k},$$

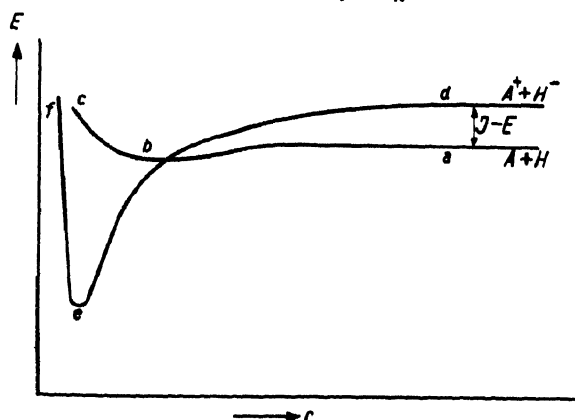


Fig. 12. Potential curves for the combinations of atoms  $A$  and  $H$  and ions  $A^+$  and  $H^-$  in the case of a compound, forming ionic molecules.

where  $r$  is the distance between the atoms,  $\alpha_i$  and  $\alpha_k$  are the polarizabilities, and  $I_i$  and  $I_k$  characteristic energies. For  $I_i$  and  $I_k$  the ionization energies (§ 11) may in general be used.

### (e) Ionic molecules

The manner in which two atoms will finally combine to form a molecule depends entirely upon the question, as to which nature of bond in the case under consideration gives the greatest decrease of energy content for the system. For example, an alkali metal atom  $A$  and a halogen atom  $H$  can combine as atoms by means of the van der Waals forces. In

\* F. London, *Z. phys. Chem. B*, 11, 246 (1931).

that case, however, the energy by which they are bound is small, the potential curve (curve *abc* in Fig. 12) is very flat. If ions  $A^+$  and  $H^-$  are formed from the alkali metal atom and the halogen atom, the ionization energy of the alkali metal atom  $I$  must be supplied to the system, and the electron affinity of the halogen atom  $E$  will be gained. Since  $I$  is usually larger than  $E$ , energy must in the end be supplied, and we are dealing with an energy level  $d$  higher than  $a$ . When, however, the two ions attract each other and an ionic molecule is formed, a large energy of combination will be gained. The curve *def* is thus a potential curve with a distinct minimum  $e$ , which is lower than

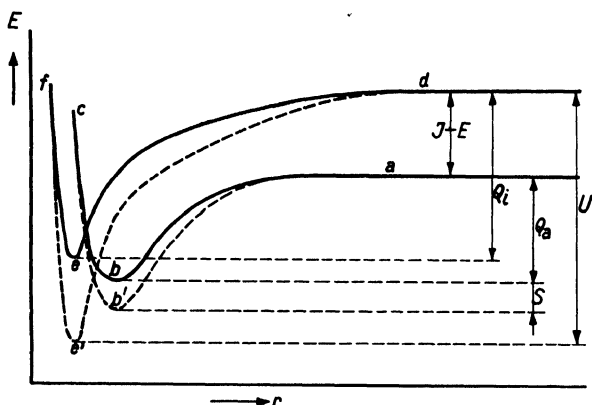


Fig. 13. Potential curves for a compound, forming atomic molecules in the gaseous state, but consisting of ions in the solid state.

the minimum  $b$  of the curve *abc*. In this case the atoms  $A$  and  $H$  have formed the ionic compound  $A^+H^-$ . The separate gaseous molecules of the alkali and alkaline earth halides are ionic molecules.

#### (f) Atomic molecules

The minimum of the potential curve for the atomic compound may, on the other hand, be lower than that of the curve for the ionic compound. When this is so the atoms will form an atomic molecule, as with the gaseous molecules of the vapours of silver and thallium halides. Here the energy of combination of the ions  $Q_i$  (see Fig. 13), decreased by the amount  $I - E$ , is less than the energy of combination of the atoms  $Q_a$ .

If we consider instead of the gaseous molecules the solid

substances (broken lines in Fig. 13), then in the case of the atomic compounds the energy of combination is increased by the energy of sublimation  $S$  of a molecular lattice, usually a small amount, while in the case of the ionic compounds, starting from the energy level  $M^+ + H^-$ , the whole lattice energy is gained, an amount considerably greater than  $Q_i$ . Thus it can happen that for the solid compound the minimum of the ionic curve again is lower, so that the molecule under consideration in the vapour state is built up of atoms, and in the solid state of ions. In the condensation of the vapour to the solid lattice we go from point  $b$  in our figure to point  $e'$ . In some cases the minima  $e$  and  $e'$  may be on the right of  $b$  and  $b'$ , since the sum of ionic radii may be greater than the sum of atomic radii.

#### § 14. Adsorption of ions.

##### (a) *Adsorption of ions in the process of the growing of crystals*

When an ion of an aqueous solution comes into contact with the surface of a salt, it can be attracted by the components of that surface and held fast for a shorter or longer time. We then say that the ion is adsorbed. The "hydration shell", i.e. the layer of water dipoles which always occurs about that ion, can hereby either remain intact or be partially pushed aside.

As a result of this adsorption, when the ion is identical with one of the ions of the salt itself, it can at a definite spot on the surface of the salt become part of that salt, and thus contribute to the growth of the crystal, provided that the same process occurs with the other components of the crystal.

##### (b) *Adsorption of ions in colloid chemistry*

If this latter condition is not fulfilled, then the surface of the salt will become charged by the ions. The phenomena of flowing potentials and electroendosmosis are dependent upon this fact. If the salt crystals are very small, of microscopic or ultramicroscopic dimensions, we are then concerned with the phenomena of colloid chemistry.

The electrical charging of colloidal particles can be brought about not only by ions which are identical to some of the ions of the salt surface, but also by ions of isomorphous salts. Thus

it is not only possible to form negatively charged colloidal silver iodide by allowing it to adsorb a small excess of iodine ions as "charging ions", but also by allowing the adsorption of chlorine or bromine ions.\*

(c) *The electric field above a crystal surface*

By the action between the positive and negative ions on the surface of the salt, a very strong electric field occurs, but only in the direct neighbourhood of the surface. The strength of this field decreases very quickly with increasing distance from the surface,† so quickly, in fact, that it can be practically neglected at a distance equal to the lattice separation  $a$  (in sodium chloride this is the distance between two Na ions or two Cl ions in the lattice). Hückel‡ proved that the field directly above an ion on the surface can still be expressed by the equation

$$E_f = \frac{\epsilon}{r^2},$$

but that at a distance  $r = \frac{1}{2}a$  from

the surface, this equation must be replaced by the following:

$$E_f = \frac{\epsilon}{a^2} \cdot 2\pi \cdot 16 \cdot e^{-2\pi\sqrt{2}\frac{r}{a}}.$$

From this distance the field decreases according to a negative power of  $e$ , and is practically zero at a distance  $r = a$ . In Fig. 14 the field above a sodium chloride surface is represented.

The van der Waals attractive forces act in general at a

\* H. R. Kruyt and P. C. van der Willigen, *Z. phys. Chem.* **139**, 53 (1928).

† See O. Blüh and N. Stark, *Z. Phys.* **43**, 575 (1927); J. E. Lennard-Jones and B. M. Dent, *Trans. Faraday Soc.* **24**, 92 (1928); J. H. de Boer, *Proc. Acad. Sci. Amst.* **31**, 906 (1928).

‡ E. Hückel, *Adsorption und Kapillarkondensation*, p. 126, Leipzig (1928).

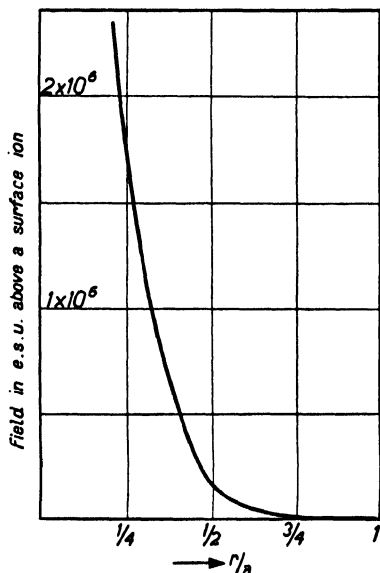


Fig. 14. Force of electric field above a surface ion of a 100-plane of NaCl. In the case of NaCl:  $a = 5.63 \text{ \AA}$ .

greater distance than the electrostatic forces which originate at the surface, so that even in the adsorption of an ion, the ion will first be held by van der Waals' forces, and only upon a closer approach to the surface will the electrostatic forces of the surface begin to play a part. Because of the rapid decrease of the electrostatic field of a salt surface, the bond between an ion above a plane surface of a salt and that surface is very weak. A chlorine ion at a distance  $r = 2.81 \text{ \AA.}$  above a sodium ion in a cube face of sodium chloride, i.e. at the normal distance between chlorine and sodium in the crystal, is bound only by an energy\*

$$Q_{100} = 0.0662 \frac{\epsilon^2}{r}.$$

This energy is different for different crystal planes, but it is always very small in comparison with that which is exerted upon a chlorine ion within the lattice

$$Q_0 = 1.7474 \frac{\epsilon^2}{r}.$$

(d) *Active places*

The bond is much stronger at the edges and especially at the corners of the crystal than in the middle of a plane surface. If the ion is added to a cube next to a layer in the process of being formed, and in a row which is partially completed (point A in Fig. 15), exactly half of the energy  $Q_0$  will be gained, so that if a gram molecule of ions ( $2N$  ions,  $N = \text{Avogadro's number, } 6.06 \times 10^{23}$ ) is added to the crystal, exactly

$$2N \frac{Q_0}{2} = N Q_0 = U,$$

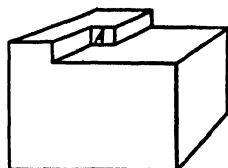


Fig. 15. By addition of an ion in point A, the energy  $Q_0$  will be gained.

thus the lattice energy is gained. Such places in the crystal as well as all the edges and corners are "active" places in contrast to those positions in the middle of a plane salt surface.

In crystallization experiments, for example, in the crystallization of sodium nitrate on cleavage planes of calcite crystals,

\* W. Kossel, *Quantentheorie und Chemie*, 1er Vortrag, herausgegeben von Falkenhagen, Leipzig (1928); I. Stranski, *Z. phys. Chem.* **136**, 259 (1928).



the first ions are added in the neighbourhood of surface inequalities, which are usually composed of layers of other ions, broken off to give a step formation (similar to Fig. 15). At the corners and edges of this step formation sodium nitrate crystallizes out with its ions similarly oriented. More nuclei for crystallization are found on fresh cleavage planes\* and the crystallization proceeds more rapidly than upon crystals which are aged, and where the most active places on the surface have already disappeared.

By the adsorption of radioactive ions on crystal surfaces Hahn† was able to confirm photographically the fact that the adsorption takes place at the edges of the crystals.

The charging iodine ions on colloidal silver iodide particles are adsorbed only at the edges and corners of the tiny crystals.‡ Freshly prepared particles of AgI have a rather irregular shape, and therefore a relatively large number of edges and corners. After a certain length of time, which is shorter according as the temperature is higher, the particles become more uniform and regular in shape without increasing in size, and the number of iodine ions adsorbed decreases sharply.

It has been necessary to go into some detail about these phenomena, because we shall later on in this book repeatedly meet analogous cases. It will in all these cases be noted that active places play a very important part in the adsorption on the surfaces of halides, oxides, and of dielectrics in general.

Adsorption of ions can occur not only directly out of solution, but also as an adsorption of atoms or molecules when these atoms either give up their electrons to the salt or lose them by emission. It also occurs when adsorbed molecules react with the ions of the salt surface. We shall repeatedly meet examples of all these cases.

### § 15. Adsorption caused by dipole attraction.

In § 13 we noted that molecules possessing a permanent electric dipole can be oriented and attracted by an electric

\* I. Stranski, *Z. phys. Chem.*, Bodenstein Festband, p. 230 (1931).

† O. Hahn, *Z. angew. Chem.* **43**, 871 (1930).

‡ E. J. W. Verwey, *Proc. Acad. Sci. Amst.* **36**, 225 (1933).

field. The same result may be brought about by the surface ions of a halide or an oxide, and a layer of adsorbed molecules is formed in which the molecules all have a very definite position in relation to the surface.

Since, as we have already seen in the previous section, the electric field of a salt surface decreases very rapidly with increasing distance from the surface, molecules whose dipoles lie sufficiently close to the surface of the molecule will be especially important in such adsorption phenomena. Such "peripheral" dipoles occur, besides in the cases of water and ammonia, especially among the organic hydroxyl compounds, i.e. alcohols, phenols, acids, and also among the organic amines. In all these substances the positive end of the dipole is nearest the surface, and it is therefore in the negative ions of the salt surface that the adsorption forces originate. When the electric field of the surface at the point where the dipole is situated is equal to  $E_f$ , the dipole whose moment is  $\mu$  is bound by an energy

$$Q_\mu = E_f \mu.$$

Due to these adsorption forces every salt surface which has been exposed to the air is covered with an adsorbed film of water. Whenever a salt is able to form a hydrate, that is to say, whenever it can take up within the crystal lattice in a stoichiometric relation one or more molecules of water per ion of the salt, the forces of attraction between the ions and the water dipoles can partially overcome the opposing lattice energy. Since the molecules of water can occupy places in the salt lattice, the ions of the salt must be pushed apart to a certain degree. If the lattice energy of a certain chemical compound is so great that the hydration forces of the ions are unable to supply the necessary energy for this "opening" of the lattice, the salt will not form a hydrate. In such a case, the hydration of the surface, i.e. the formation of an adsorbed layer of water molecules, will be especially strong, since a large lattice energy indicates ions with high charge or small volume, which in their turn give especially strong ionic fields. It is thus easy to understand why a salt like  $\text{CaF}_2$ , which can form no hydrate and is practically insoluble, is

nevertheless covered by a monomolecular film of water so strongly bound to the surface that it is impossible to remove it at ordinary temperatures.\* Keeping the substance for months in a high vacuum over  $P_2O_5$  does not remove the adsorbed molecules. Under the action of heat the water molecules react with the fluorine ions of the  $CaF_2$  surface upon which the molecules are adsorbed, whereby HF escapes and the adsorbed  $H_2O$  molecules are replaced by  $OH^-$  ions which are adsorbed by the surface of  $CaF_2$  now freed by its fluorine ions. The  $OH^-$  ions in turn lose water and give  $O^{--}$  ions (see Fig. 16).

On the other hand a salt like  $BaCl_2$ , which easily forms a hydrate  $BaCl_2 \cdot 2H_2O$ , and is easily soluble, has its surface

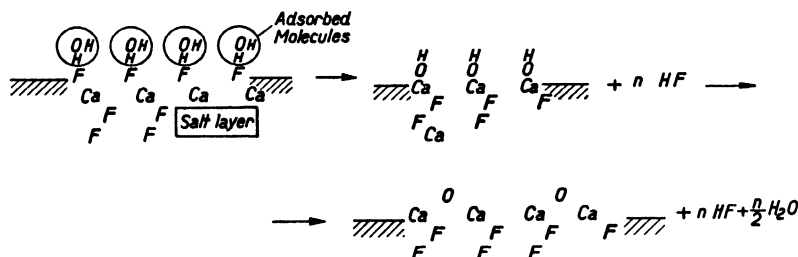


Fig. 16. Adsorbed water molecules react with the surface of  $CaF_2$ , forming HF and adsorbed oxygen ions.

covered with adsorbed water molecules, but gives up these water molecules much more easily.

Active places on the salt surface which are of great importance in the adsorption of ions, are of much less importance in the adsorption of dipoles. The attraction of a dipole for an ion is dependent not only upon the distance, but also upon the angle which the dipole makes with the line joining the ion and the dipole. If we let this angle equal  $\psi$  (Fig. 17), the energy of combination between a dipole with a moment  $\mu$  and an ion with a charge  $\epsilon$ , at a distance  $r$ , is given by

$$Q = \frac{\epsilon\mu}{r^2} \cos \psi.$$

\* J. H. de Boer and C. J. Dippel, *Z. phys. Chem. B*, **25**, 399 (1934).

This energy is at a maximum when the dipole is in such a position that  $\psi = 0^\circ$ , is zero when  $\psi = 90^\circ$ , and becomes negative when  $\psi > 90^\circ$ . In the last position the dipole is repulsed by the ion.

The action of the surrounding ions upon a dipole, adsorbed on a given ion, is thus much smaller than that of the ion upon which the dipole is adsorbed, not only because the energy decreases with the square of the distance, but also because the dipole is in an unfavourable position with respect to the surrounding ions.

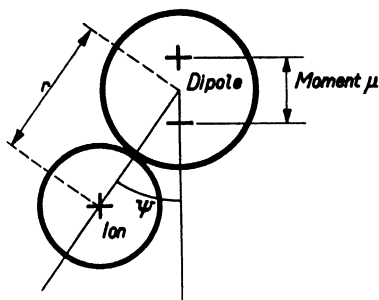


Fig. 17. A dipole with a moment  $\mu$  at a distance  $r$  from an ion is bound by this ion. The energy  $Q = \frac{\epsilon\mu}{r^2} \cos \psi$  also depends on the angle  $\psi$ .

The activity of the projecting edges or corners of a salt surface is much less noticeable than in the adsorption of ions because of the above facts. Re-entering angles or cracks and depressions in the surface can even have a distinctly unfavourable influence on the adsorption of dipoles.

#### § 16. Adsorption caused by electrostatic polarization and van der Waals' forces.

If a molecule with a polarizability  $\alpha$  is situated at a distance  $r$  above a surface whose electric field equals  $E_f$  at that point, the molecule will be polarized and attracted; the energy of combination is

$$Q_\alpha = \frac{E_f^2 \alpha}{2}.$$

When the surface of the salt is plane and has no active places, this electrostatic polarization gives rise only to weak energies of combination, and is always exceeded by the van der Waals attractive forces.\* On a plane salt surface the van der Waals adsorption forces are, however, in turn usually exceeded by the dipole forces of attraction if dipoles are present,† especially when the dipoles are situated very near the surface of the molecules (see above).

\* J. E. Lennard-Jones and B. M. Dent, *Trans. Faraday Soc.* **24**, 92 (1928).

† F. V. Lenel, *Z. phys. Chem. B*, **23**, 379 (1933); J. H. de Boer and J. F. H. Custers, *Z. phys. Chem. B*, **25**, 225 (1934).

The energy of combination which results from the van der Waals attractive forces is also proportional to the polarizability  $\alpha$ . London\* deduced, as we have already seen in § 13, the following approximation formula for the reciprocal energy between two atoms  $i$  and  $k$ :

$$Q_{ik} = \frac{3}{2} \cdot \frac{\alpha_i \alpha_k}{r^6} \cdot \frac{I_i I_k}{I_i + I_k} = \frac{C}{r^6}.$$

Since the van der Waals energies are additive, the adsorption energy of a given atom or molecule on the surface can be found by adding the reciprocal energies between the atom or molecule and all the atoms of the adsorbent. As the reciprocal energies decrease in inverse proportion to the sixth power of the distance, such a summation series converges quite rapidly.

If instead of making the summation one integrates over the whole volume of the adsorbent, one obtains the expression

$$Q_w = \iiint \frac{C}{r^6} \cdot N_1 \cdot dv = \frac{N_1 \pi C}{6} \cdot \frac{1}{d^3},$$

where  $d$  is the distance of the atom to the surface, and  $N_1$  is the number of atoms of the adsorbent per cubic centimetre. This energy then decreases in inverse proportion to the third power of the distance to the surface.†

For a surface such as that of carbon, which is not built up of ions, the van der Waals forces are the only forces which give rise to adsorption. The above-mentioned expression gives, however, values for the adsorption energy of He, A, CO, CO<sub>2</sub>, etc. on carbon which are too small.‡

The surface of carbon may not as a matter of fact be considered plane, since it has many depressions and channels of molecular dimensions. In these depressions the energy of combination, thanks to the van der Waals forces, is much greater than on a plane surface.§ In such an arrangement as is represented in Fig. 18 the energy is *four* times that on a plane surface, while an arrangement as in Fig. 19 gives *six*

\* F. London, *Z. Phys.* **63**, 245 (1930); *Z. phys. Chem. B*, **11**, 246 (1931).

† M. Polanyi and F. London, *Naturwissenschaften*, **18**, 1099 (1930).

‡ J. H. de Boer and J. F. H. Custers, *Z. phys. Chem. B*, **25**, 225 (1934).

§ Cf. also M. Polanyi, *Trans. Faraday Soc.* **28**, 316 (1932).

times that energy, and the theoretically calculated adsorption energy is of the same order of magnitude as that found experimentally.\*

The same fact is true for the surfaces of other substances, namely, that the van der Waals adsorption is strong at re-entring angles, depressions and cracks, while at projecting corners, edges or points of the surface this force is especially weak. In the latter places the electrostatic influence is large, so that at such active places of the salt surface the electrostatic polarization is able to exceed by far the van der Waals adsorption forces.\*

Besides the characteristic difference just treated between the electrostatic and van der Waals polarization there are still two important points of difference to be noted.

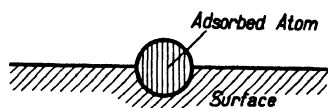


Fig. 18. An atom is adsorbed in a flat hole of molecular dimensions in the surface.

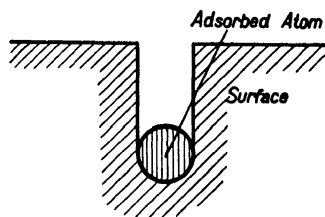


Fig. 19. Adsorption at the bottom of a capillary of molecular dimensions.

Because of the fact that the van der Waals forces reach a maximum when the adsorbed atom is directly in contact with as many atoms or ions of the surface as possible, the adsorbed atoms will be situated above the middle of the elementary cells of the surface, that is, *between* the ions of the surface and not above one of them.† On the other hand, electrostatic polarization favours the position just above the ions, since in that position the electric field of the surface is at a maximum. Thus in the adsorption on a salt surface the adsorbed atoms will be situated, in the active places, upon the ions, and in other places, between the ions.

\* J. H. de Boer and J. F. H. Custers, *Z. phys. Chem. B*, **25**, 225 (1934).

† Cf. J. E. Lennard-Jones, *Trans. Faraday Soc.* **28**, 333 (1932).

Since atoms adsorbed by means of the van der Waals forces also attract each other by means of these same forces, in this type of surface there will be a tendency toward agglomeration on the surface. The agglomeration is of course opposed by changes in the temperature, so that in this two-dimensional layer adsorbed on the surface phenomena occur which are analogous to the ordinary condensation and sublimation of solids. We may here speak of two-dimensional condensation and evaporation, since the forces between the adsorbed atoms are actually of the same nature as those which cause condensation in atomic or molecular lattices (not in ionic lattices). The only difference is that all the atoms, whether in the two-dimensional solid or two-dimensional gaseous layer, are bound to the surface by van der Waals' attractive forces. There are certain indications which even allow one to distinguish between a two-dimensional solid layer and a two-dimensional liquid layer.

The formation of the above-mentioned agglomerated regions is naturally favoured by low temperatures and high surface concentrations, and is also greater when the adsorbed substance is one which has a high energy of vaporization in the solid or liquid state.

Atoms adsorbed by electrostatic polarization possess induced dipoles, which, when they are similarly oriented, repel each other. This is again very different from the case of atoms adsorbed by means of van der Waals' forces.

The following summary gives the differences between the two types of adsorption:\*

*Van der Waals' adsorption*

The adsorption is at a maximum in depressions, cracks, and re-entering angles, and at a minimum on projecting angles, edges and points. On a plane surface this adsorption exceeds the adsorption due to electrostatic polarization. Adsorbed atoms have their position over the centre of the elementary cells of the surface components. Adsorbed atoms exert an attraction for each other.

*Adsorption caused by electrostatic polarization*

The adsorption is at a maximum at projecting angles, edges and points of the surface.

At active places this adsorption may be stronger than the van der Waals adsorption.

Adsorbed atoms have their position directly over the ions of the adsorbing surface.

Adsorbed atoms repel each other.

\* J. H. de Boer and J. F. H. Custers, *Z. phys. Chem. B*, **25**, 237 (1934).

### § 17. Dipole adsorption on a water surface.

The saturated hydrocarbons are practically insoluble in water, since the hydration energy of these dipole-free molecules is too small, and the energy necessary to separate some of the water molecules from each other in order to make room for the hydrocarbon molecule is too high. They do, however, spread themselves out over a water surface, whereby the hydrocarbon chains must be imagined to lie flat on the surface, since it is in this position that the van der Waals force of attraction is the greatest. Research by Cassel and Formstecher\* has indeed shown that the hydrocarbon molecules are adsorbed in a flat position on the water surface, and moreover that these adsorbed molecules attract each other as we should expect according to § 16. Upon the hydrocarbon molecules lying directly on the surface other hydrocarbon molecules add themselves, since the molecules also attract each other by van der Waals' forces. In this way the usual film of liquid hydrocarbons is formed on water.†

If, however, there is a polar group in the end position on the hydrocarbon, as for example  $\text{—COOH}$ , or in other words if the substance is a fatty acid, then the behaviour is quite different. The hydration energy of this carboxyl group is very great, which makes the fatty acids, especially the lower ones such as acetic acid, very soluble in water. With the higher fatty acids, as stearic or palmitic acid, this is no longer the case, although the  $\text{—COOH}$  groups, because of their forces of hydration, are still quite tightly bound to or in the water surface.‡

If there are only a few fatty acid molecules present on the surface, then the carboxyl groups will be directed into the water, while the hydrocarbon remainder of the molecule lies flat on the surface of the water. With respect to each other the molecules behave as in the two-dimensional gaseous state discussed in the previous section. At high concentrations on

\* H. Cassel and M. Formstecher, *Kolloidzshr.* **61**, 18 (1932).

† Oils having more than eight carbon atoms in the molecule do not spread on a water surface, but form lenses, cf. W. D. Harkins, *Colloid Symposium Monograph*, **6**, 26 (1928); I. Langmuir, *J. chem. Phys.* **1**, 756 (1933).

‡ I. Langmuir, *J. Amer. chem. Soc.* **38**, 221 (1916); **39**, 1848 (1917).



the surface such as can be brought about by lateral compression the molecules take a standing position, that is to say the carboxyl groups remain as before, directed into the water, but the hydrocarbon remainders are pushed away from the water and stand parallel to each other,\* at the same time exerting an attraction on each other due again to their van der Waals forces.

The carboxyl groups are partially dissociated, so that some of the hydrogen ions are relatively mobile under the monomolecular fatty acid layer. The result is that the liquid possesses a greater electric conductivity just under the surface than deeper in the liquid.†

Other molecules possessing dipoles can also exhibit this phenomenon of spreading out in a monomolecular layer with the dipoles always directed toward the water.

Water dipoles fasten themselves upon and between the dipoles of the adsorbed molecules. If in addition there are ions present in the water these ions will also be attracted to some extent, and to some extent repelled, which will give rise to a diffuse ionic double layer, similar to those which play such an important part in colloid chemistry.

### § 18. The change of potential due to a dipole layer.

An important device in the study of monomolecular films of fatty acids on water and similar phenomena is the measurement of the difference of potential between the liquid and an electrode above the liquid. This difference of potential can be measured by making the air gap between the metal electrode and the water surface conductive by means of some radioactive substance.‡

After the formation of a monomolecular film of a fatty acid or of some other substance having a dipole, this potential difference will be found to be changed. When a number of dipoles is more or less regularly arranged in a plane there is

\* For further details refer to E. K. Rideal, *An Introduction to Surface Chemistry*, Chap. III, Cambridge University Press, 2nd ed. (1930).

† J. W. McBain and C. R. Peaker, *Proc. roy. Soc. A*, 125, 394 (1929).

‡ J. Guyot, *Ann. Phys.*, Paris (10), 2, 508 (1924).

a difference of potential between the two portions of space which are separated by this dipole plane.

Since this difference of potential will later prove to be of great importance to us, it is necessary to go into it in some detail at this point. If one considers an infinitely large plane surface occupied at regular intervals by positive charges (Fig. 20 gives diagrammatically a cross-section of such a surface), then an electron will experience an attractive force from this surface which is independent of the distance of the electron from the surface. At point *A* as well as at point *B* or any other point chosen at such a distance that the charge can be considered to be distributed homogeneously, the force can be represented by  $F = 2\pi\sigma\epsilon^2$ ,



Fig. 20. Force on an electron in *A* and in *B* is the same; force independent of distance.

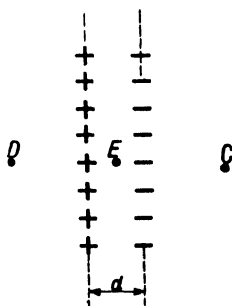


Fig. 21. Force on an electron in *C* and *D* is zero.

where  $\sigma$  represents the number of charges per unit of surface (for instance per square centimetre).

If at a distance  $d$  from the positive surface a negatively charged surface is placed, which also contains  $\sigma$  charges per square centimetre, then the electron at point *C* (Fig. 21) will be attracted by the positive surface by a force  $F$ , but repelled by the negative surface by an equal force  $F$ , so that the total resulting force on the electron will be zero. Similarly the force at point *D* is equal to zero. On the other hand at point *E* an electron experiences a force toward the left from the positive surface, and an equal force in the same direction from the negative surface, so that the total force exerted is  $2F$ , where

$$2F = 4\pi\sigma\epsilon^2.$$

This is valid for all points between the two surfaces. If an electron is moved from  $C$  to  $D$ , a constant force will be exerted on the electron at all points between the planes and there will be a gain in energy

$$2Fd = 4\pi\sigma\epsilon^2d.$$

This means that between the points  $C$  and  $D$ , or in general between all points to the right of the two charged planes and all points to the left of the planes, there is a sudden change in potential

$$\Delta V = 4\pi\sigma\epsilon d.$$

If we now consider our arrangement of two planes as one dipole plane, which contains  $\sigma$  dipoles per square centimetre,

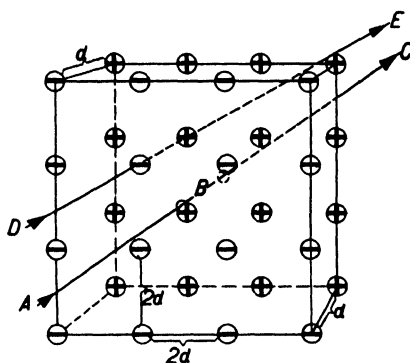


Fig. 22. Two planes of charges; distance  $d$ ; distance of the charges in the planes  $2d$ . Line  $ABC$  passes through the planes between the charges. Line  $DE$  passes through the planes at points occupied by charges.

each with a moment  $\mu = \epsilon d$ , then the change in potential can be written

$$\Delta V = 4\pi\sigma\mu.$$

As has already been noted, the force outside the double layer is equal to zero only when the charges can be considered to be distributed homogeneously. When, however, the distribution of charges is not homogeneous, but the dipoles are distributed in a regular two-dimensional pattern, it appears that electrical forces are already detectable at a distance from the double layer which is equal to the distance between the dipoles in the layer. If we consider, for example, a double layer as indicated in Fig. 22, in which the "dipole length" is equal to  $d$ , and the separation of the dipoles is equal to  $2d$ ,

giving one dipole per  $4d^2 \text{ cm.}^2$ , and thus  $\sigma$  equal to  $\frac{1}{4d^2}$ , then the course of the potential along the line  $ABC$  will be given in Fig. 23. Thus we see that the attraction for an electron becomes noticeable already at a distance  $2d$  (the same as the distance between the dipoles in the layer). If the electron is moved along the line  $DE$ , it meets one of the charges (an ion for example) which constitute the double layer and is thereby strongly repelled, while on the other side of the layer an attraction takes place. It would not be possible to move an electron exactly along this line through the layer.

Let us now return to the problem of monomolecular fatty acid films, where we can now understand that the formation

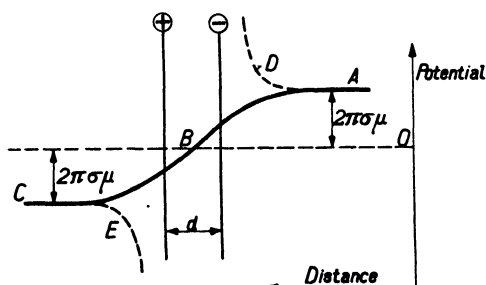


Fig. 23. Change of potential, when an electron passes through a dipole layer along the lines  $ABC$  or  $DE$  of Fig. 22. A decrease in potential in this figure means a gain of energy for an electron, i.e. a larger negative value of potential.

of such a film will change the difference in potential between the water and the metal electrode by the following amount:

$$\Delta V = 4\pi\sigma\mu_v,$$

where  $\sigma$  is now the number of molecules of fatty acid per unit of surface and  $\mu_v$  is the average vertical component of the moment of the dipoles forming the layer. Since in this case  $\mu_v$  is given by the dipole moment of the carboxyl group, decreased by that of the water molecules which have been pushed aside, and combined with that of the water molecules which are bound by hydration to the carboxyl group, the moment found in this way will be much smaller than the actual moment of the carboxyl group.\*

\* J. H. Schulman and E. K. Rideal, *Proc. roy. Soc. A*, **130**, 259, 270 (1930).

Moreover, the measured jump in potential difference is influenced by the diffuse ion atmosphere which forms under the fatty acid film. Schulman and Rideal found that the degree of this influence was not dependent on  $\sigma$ , but was very dependent on the character of the anion in solution, and on the hydrogen-ion concentration. If the jump in potential difference due to these latter causes is denoted by  $\Delta V_\mu$ , the following expression is obtained for the relation between  $\Delta V$  and  $\sigma$ :

$$\Delta V = 4\pi\sigma\bar{\mu} + \Delta V_\mu,$$

where  $\bar{\mu}$  equals the actual contribution of the carboxyl group with its water molecules.\*

The moment  $\bar{\mu}$  is still very dependent on the state of the film; it is, for example, for fatty acids in a dilute, two-dimensional gaseous state, equal to  $1.0 \times 10^{-19}$  e.s.u., in the condensed liquid state  $1.59 \times 10^{-19}$  e.s.u., and in the condensed solid state  $3.18 \times 10^{-19}$  e.s.u. In all these cases these active dipoles are placed with their positive ends directed away from the surface. The moment is thus here always much smaller than the actual moment of the carboxyl group, which equals  $1.4 \times 10^{-18}$  e.s.u., or  $14 \times 10^{-19}$  e.s.u. Another reason besides the one already given why the moment is so small here lies in the fact that the COOH group is so oriented that the vertical component of the dipole moment is relatively small.†

We must here call attention to the fact that in those states of the monomolecular films, in which the dipole moment was found constant, the measured jump in potential is actually directly proportional to  $\sigma$ .

Other substances such as the higher alcohols‡ can of course also be investigated in a similar manner.

Yamins and Zisman§ found another method of measuring  $\Delta V$  by the use of a vibrating condenser.

### § 19. Adsorption on metal surfaces.

As we have already seen in § 8 an electric charge polarizes a metal in such a way that the attractive force can be described

\* J. H. Schulman and E. K. Rideal, *Proc. roy. Soc. A*, **130**, 284 (1930).

† Cf. N. K. Adam and J. B. Harding, *Proc. roy. Soc. A*, **138**, 411 (1932).

‡ J. H. Schulman and A. H. Hughes, *Proc. roy. Soc. A*, **138**, 430 (1932).

§ H. G. Yamins and W. A. Zisman, *J. chem. Phys.* **1**, 656 (1933).

as if a charge of opposite sign were acting upon the metal surface at a distance below the surface equal to the distance above the surface of the actual inducing charge. Due to this image force, an ion will be attracted to a metallic surface by an adsorption energy

$$Q_i = \frac{e^2}{4d},$$

where  $d$  is the distance of the ion from the surface.

In a similar way dipoles will also be bound to metal surfaces.\* The energy of combination is hereby

$$Q_\mu = \frac{2\mu^2}{16d^3} = \frac{\mu^2}{8d^3},$$

where  $\mu$  is the dipole moment and  $d$  is again the distance from the metal surface. This adsorption energy is not very large; in several cases the van der Waals forces mentioned below give rise to higher energies.

Finally, neutral and dipole free atoms or molecules can be adsorbed by metallic surfaces by means of the van der Waals forces. The approximation formula of London (§§ 13 and 16) is not directly applicable here.

In the case of a metal we are not concerned with a lattice made up exclusively of positive and negative ions, or of neutral atoms, in which the components all have definite positions, so that the reciprocal forces upon the adsorbed atom due to each of the components may be added. As we have already seen in § 1 a metal consists of a lattice of positive ions, and of electrons which have no fixed positions.

It is better in this case again to consider the whole metal as a single body, just as we did in the discussion of the adsorption of ions and dipoles by metals. We must consider it as a perfectly polarizable system, where the action of the polarization can be described as an image force. The rapidly changing electric fields, which arise because of the fact that the electrons in the atom are continually changing their positions with respect to the nucleus and to each other, induce mirrored polarizations, whereby the total effect is an attraction, in exactly the same way as in the case of the van der

\* P. Debye, *Physica*, 1, 362 (1921).

Waals forces between two atoms (§ 13). Lennard-Jones\* deduced under these assumptions the following expression for the van der Waals adsorption energy of a metal in the case of a neutral, spherically symmetrical atom like a rare gas atom:

$$Q_w = \frac{\epsilon^2 \bar{r}^2}{6d^3},$$

where  $d$  denotes the distance of the atom (the nucleus of the atom) to the metal, and the quantity  $\bar{r}^2$  denotes the square of the average distance of the electron charges to the nucleus (taken over all directions:  $\bar{x}^2 = \bar{y}^2 = \bar{z}^2 = \bar{r}^2/3$ ). The quantity  $\bar{r}^2$  can be calculated from the electron distribution in an atom, or from the susceptibility of a diamagnetic atom:

$$\chi = \frac{N\epsilon^2}{6mc^2} \cdot \frac{1}{\bar{r}^2},$$

where  $\chi$  denotes the susceptibility per gram atom,  $N$  Avogadro's number ( $6.06 \times 10^{23}$ ),  $m$  and  $\epsilon$  respectively the mass and charge of an electron, and  $c$  the velocity of light.

In many cases of adsorption on a metal surface the dipole attraction exceeds the attraction due to the van der Waals forces, just as was the case in the adsorption on salt surfaces. This is especially so when the dipoles lie near the surface of the molecules.

In a similar manner the hydrocarbons may be bound to metal surfaces by van der Waals' forces, the molecules here lying flat on the surface. A second layer of molecules can be formed upon the first by the addition of other molecules in corresponding parallel positions above the first, just as was the case when we were dealing with water surfaces. Liquid hydrocarbons spread themselves out as a liquid film upon metal surfaces even better than upon water surfaces.

The molecules of fatty acids are adsorbed on metal surfaces as on water surfaces with their dipoles directed toward the surface, and they push away the molecules of the hydrocarbons. No new molecules of fatty acids can be adsorbed

\* J. E. Lennard-Jones, *Trans. Faraday Soc.* **28**, 334 (1932).

upon a metal surface which is already occupied by a monomolecular layer of fatty acid molecules, because the van der Waals forces of the hydrocarbon end of the fatty acid molecules which act in a direction away from the surface are smaller than the mutual van der Waals attractive forces of the fatty acid or hydrocarbon molecules. Thus the hydrocarbons and fatty acids do not spread out upon an already existing monomolecular layer of a fatty acid, but form lenses.

## § 20. Adsorption of alkali metal atoms on metallic surfaces.

When the atoms of an alkali metal condense to form the solid metal, they influence each other in such a way that their valence electrons become more or less free in the metal as conduction electrons in the positive-ion lattice. The same thing happens when tungsten atoms condense to solid metallic tungsten.

One may now ask what will happen when an atom of an alkali metal is adsorbed on the surface of another metal, for instance tungsten. One might then expect that the valence electron of the alkali metal would become a conduction electron and that the alkali metal atom would become an ion, surrounded like the ions of the adsorbing metal lattice by the negative charges of the electrons.

We shall see later that experiments with contact potential, thermionic emission, and photoelectric emission prove that in the adsorption of an alkali metal atom on a tungsten surface a dipole is formed which has its positive end directed away from the surface. By analogy with the above imaginary picture, this was not to be expected, the less since the addition of a tungsten atom to a tungsten surface in no way changes the double layer of that surface (see § 8). On the basis of the fact that the alkali metal atom is larger than the tungsten atom, one might, however, conceive that the nucleus of the alkali metal atom would project farther above the surface than the average negative charge, and thereby give rise to the dipole whose presence has been proved.

If our conception of the van der Waals forces is correct we may not expect any electrical asymmetry, so that other forces



must play a part in the adsorption of alkali metal atoms on metal surfaces.

As we have already seen in § 8, a metal may be compared to an atom which possesses not only an ionization energy  $I = \epsilon\phi_0$ , but also an electron affinity  $E = \epsilon\phi_0$ . When an alkali metal atom comes into contact with an electronegative atom, an ionic compound is formed, wherein the alkali metal atom gives up its electron to the electronegative atom, and the ions are bound together by means of Coulomb forces (see § 12). We may expect an analogous process in our case. If we trace the potential curve of this process we obtain, as in Fig. 24, a curve

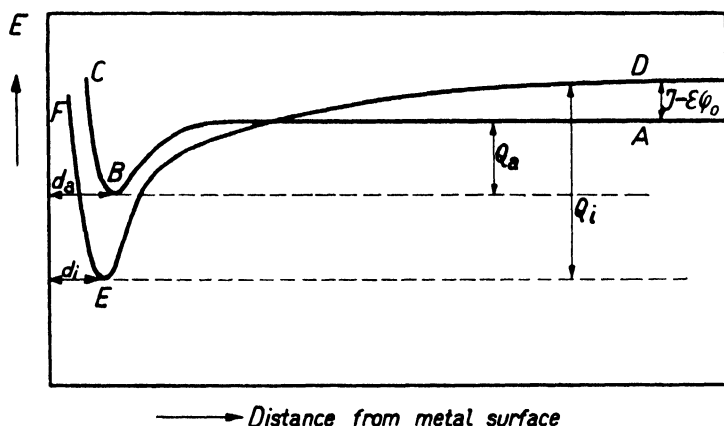


Fig. 24. Potential curves for the adsorption of atoms and ions at a metal surface.

wholly analogous to the one of Fig. 12 in § 13.  $ABC$  represents the curve of the potential due to the combining of the alkali metal as an atom with the surface, where  $Q_a$  is the adsorption energy of the atom and  $d_a$  is the distance from the metal surface. If we ionize the atom and take the electron into the metal, we must add to the system an amount of energy equal to  $I - \epsilon\phi_0$  (level  $D$  in Fig. 24). The alkali metal ion will now be more strongly attracted by the metal than was the atom ( $Q_i > Q_a$ ), and it can also approach more closely to the surface ( $d_i < d_a$ ). The result is that a surface ionic compound is here formed in a manner quite analogous to the formation of  $\text{NaCl}$  from  $\text{Na}$  and  $\text{Cl}$ .\*

\* J. H. de Boer and C. F. Veenemans, *Physica*, 1, 753 (1934).

It may of course happen that the quantity  $I - \epsilon\phi_0$  is negative, as in the system caesium on tungsten, where  $I = 3.88$  electron volts and  $\epsilon\phi_0 = 4.52$  electron volts. In this case the level  $D$  is lower than the level  $A$ , as is also true of the caesium and fluorine system, where  $I = 3.88$  electron volts and  $E = 4.1$  electron volts. We shall see in § 29 that in such cases the caesium evaporates at high temperatures from the tungsten quantitatively in ionic form.

### § 21. Adsorption of such gases as hydrogen and oxygen on metals.

Since a metal may take the part of the electropositive component in the formation of an ionic compound, it is possible that, by the adsorption of electronegative gases like oxygen and the halogens for instance, these elements may be bound to the surface as negative ions. In such a case we may speak of a *surface halide* or a *surface oxide*. The phenomenon of the formation of surface oxide films is of extremely great importance in the chemistry of the metals. We wish expressly to point out here that we are not concerned in these cases with oxide layers of several molecular diameters thickness, such as are obtained by electrolytic oxidation or by chemical passivation, but exclusively with the adsorption of a monomolecular layer on a surface.

In order that the adsorption of ions may take place, the adsorption energy of the ions must be greater than the adsorption energy of the atoms increased by the quantity  $\epsilon\phi_0$  and decreased by the electron affinity of the atom. When we are concerned with a double negative ion, as is probably the case with oxygen, the quantity  $\epsilon\phi_0$  must be multiplied by 2, and the electron affinity is negative (see § 11).

Since, in forming such a surface oxide layer, we start from the molecules, the dissociation energy of the molecules into atoms must still be supplied. We shall see later that the surface tungsten atoms must here be considered to play the part of positive ions as in a chemical compound, and that the case is one of pure chemisorption.

Hydrogen is adsorbed on many metal surfaces as an atom

rather than as a molecule, when the temperature is not too low, while at very low temperatures it is adsorbed as a molecule with a much smaller energy of adsorption.\* This behaviour has been known as "activated" adsorption since the work of Taylor.† In such a case the adsorption energy of the atom must exceed that of the molecule increased by the dissociation energy of the molecule (all the energies being calculated per atom). Lennard-Jones showed by means of potential curves (Fig. 25) that at low temperatures no adsorption of atoms could be expected to take place, but only an adsorption of

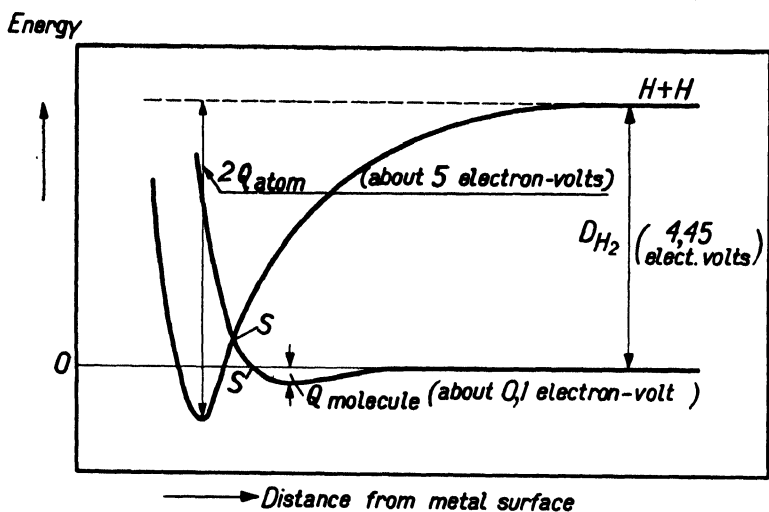


Fig. 25. Potential curves for the adsorption of hydrogen molecules and hydrogen atoms at a metal surface.

molecules, because the molecules have not sufficient energy to pass beyond the point *S*. The distance of *S* above the zero axis *SS'* may be called the energy of activation.‡

The solution of gases in metals and the diffusion of gases through metals is closely connected with the adsorption phenomena of gases on metal surfaces. The heat effect, for example, which can be measured by the dependence on

\* A. F. Benton and T. A. White, *J. Amer. chem. Soc.* **52**, 2325 (1930).

† H. S. Taylor, *J. Amer. chem. Soc.* **53**, 578 (1931), and several later articles. Cf. also H. S. Taylor and A. Sherman, *Trans. Faraday Soc.* **28**, 247 (1932).

‡ J. E. Lennard-Jones, *Trans. Faraday Soc.* **28**, 341 (1932).

temperature of the diffusion of hydrogen through metals as nickel and platinum, is given by the energy of desorption from the surface from which the hydrogen must be evaporated.\*

Experiments by Coehn and his collaborators† show that hydrogen is present in palladium (also in iron and nickel‡) at least partially in the form of protons, thus as positive ions. We may, therefore, expect that in similar cases hydrogen exists as positive ions on the surface of the metal. We shall see later (§ 48) that the thermionic emission and the photoelectric phenomena actually support this assumption.

\* Cf. the experiments of W. R. Ham, *J. chem. Phys.* **1**, 476 (1933).

† A. Coehn and W. Specht, *Z. Phys.* **62**, 1 (1930); A. Coehn and H. Jurgens, *Z. Phys.* **71**, 179 (1931).

‡ T. Francini (1931), cited by J. Franck, *Nachr. Ges. Wiss. Göttingen*, p. 293 (1933).

### CHAPTER III

## THE ADSORPTION OF CAESIUM ON TUNGSTEN SURFACES

### § 22. Introduction.

In 1923 Langmuir and Kingdon\* described several experiments in which a tungsten filament was heated in caesium vapour. Metallic caesium was kept at 25° C. in a previously evacuated tube, so that at room temperature the caesium vapour was saturated. In this tube a tungsten filament could be heated to various temperatures surrounded by the caesium vapour, while at the same time it could be given a positive or negative potential with respect to a surrounding cylinder. Under this treatment the tungsten filament became covered with a relatively tightly bound layer of adsorbed caesium, which could not be removed by heating it to above 300° C.

The electron emission of such a caesium-covered tungsten filament is much higher than that of a clean tungsten filament, and it is from the study of this electron emission that our knowledge of the state of such adsorbed layers has arisen. Measurements of contact potential (§ 10) show that the filament covered with caesium is positive with respect to a clean tungsten filament. A preliminary measurement of the Richardson work function (§§ 2 and 7) gave a value  $\phi_0 = 1.38$  volts, while the value for pure tungsten is 4.52 volts. This shows that the adsorption of caesium on the tungsten surface has caused the formation of an electrical double layer, whose *positive side is directed away from the surface*. We have already seen in § 18 that such an electrical double layer gives a jump in potential which in this case lowers the work function.

In their first articles Langmuir and Kingdon considered that in the formation of such a double layer the caesium gave up its valence electron to the tungsten, and was bound to the metal as an ion by means of the image force. As a condition for such an adsorption they considered it necessary that the

\* I. Langmuir and K. H. Kingdon, *Science*, **57**, 58 (1923).

ionization energy of the caesium ( $I = 3.88$  electron volts) should be less than the electron affinity of the metallic tungsten (§ 8;  $\epsilon\phi_0 = 4.52$  electron volts). In our discussion in § 20 we saw that this condition, although not essential, is very favourable.

The conception that the positive caesium ions with their mirror images form the electrical double layer is maintained in principle by Langmuir and his collaborators in later articles, but in these articles, as we shall see later, no distinction or only a very vague distinction is made between adsorbed atoms and adsorbed ions. In the work of Becker, however, to which we shall repeatedly refer, this distinction is indeed made. The conception which will be developed in this book coincides to a great extent with that of Becker, although several very essential points of difference must be indicated. To mention only one of these points here, Becker ascribes the lowering of the work function exclusively to ions, while through the development of our conception of adsorption we shall ascribe a very important part in this phenomenon to atoms also.

### § 23. The ionization of caesium on a hot tungsten filament.

When a tungsten filament is heated to a high temperature (above  $1200^\circ \text{K.}$ ), in caesium vapour, and at the same time made positive with respect to a surrounding metal cylinder, all the caesium atoms striking the filament are ionized and evaporated as positive ions toward the negatively charged cylinder. In order that quantitative ionization shall take place, it is necessary that the ionization energy of the atom be smaller than the electron affinity of the metal, which condition, as we have seen in the previous section and in § 20, is fulfilled in this case. Inspection of Fig. 24 in § 20 shows us directly that the energy of vaporization of the adsorbed ion as such (difference in height between the minimum of the potential of the ion curve and the horizontal part of the same curve) is smaller than the energy of vaporization of the adsorbed ion in the form of an atom (difference in height between the minimum of the potential of the ion curve and the horizontal part of the atom curve), only when the horizontal part of the

ion curve is lower than the same part of the atom curve, or when  $I < \epsilon\phi_0$ . In the case of sodium on tungsten, which is represented schematically in Fig. 24 in § 20, the adsorbed ions will evaporate mainly in the form of atoms; in the case of caesium or rubidium on tungsten, positive caesium or rubidium ions evaporate from the tungsten wire. Thus the circumstance that atoms evaporate from a filament does not mean that these atoms were adsorbed as such, while, conversely, it is reasonable to suppose that in some cases an adsorbed atom may evaporate in the form of an ion.

We have seen in the previous section that the work function of tungsten is lowered by the adsorption of caesium on its surface. The decrease in work function proceeds as the surface of the tungsten becomes more completely covered with adsorbed ions, until at a given moment the electron affinity is equal to, and thereafter less than, the ionization energy of the caesium atom. From this moment the evaporation in the form of atoms exceeds that in the form of ions, and when the work function is lowered still more, that is, when the surface is occupied by a still greater amount of adsorbed ions, they evaporate practically exclusively in the form of atoms.

As we shall see later (§ 33) the work function of tungsten can be lowered by other means, for example, by the adsorption of thorium on the tungsten surface. In this case, where  $\phi$  is reduced from 4.52 to 2.69 volts, heating the filament in caesium vapour caused no evaporation of caesium as caesium ions. When  $\phi$  was raised very much by the adsorption of oxygen (§ 46) to 9.2 volts, Langmuir and Kingdon\* found that at high temperatures copper atoms were as a matter of fact ionized ( $I = 7.69$  electron volts), while this was not the case with mercury atoms ( $I = 10.39$  electron volts).

At sufficiently high temperatures, when the filament is practically clean, all the caesium atoms on a tungsten filament are ionized and the ions are evaporated. A rise in the temperature of the filament then gives no rise in the ion current, since this current is entirely dependent on the number of caesium atoms which strike the filament per second. This

\* I. Langmuir and K. H. Kingdon, *Proc. roy. Soc. A*, **107**, 61 (1925).

number of atoms depends, besides on the dimensions of the wire, also on the vapour pressure, to which it is directly proportional. Conversely, it is possible to calculate the vapour pressure from the positive-ion current by means of the formula

$$p = \frac{i \sqrt{2\pi m_i k T}}{\epsilon},$$

where  $p$  is the required vapour pressure in bars (1 bar = 1 dyne per cm.<sup>2</sup> =  $10^{-6}$  atm.),  $i$  is the positive-ion current in amp./cm.<sup>2</sup>,  $m_i$  is the mass of a caesium ion,  $k$  is Boltzmann's constant,  $T$  the absolute temperature and  $\epsilon$  the charge on a singly charged positive ion. Langmuir and Kingdon\* determined the vapour pressure of caesium at various temperatures in this manner, keeping the filament temperature in each case at 1500° K. From their measurements they derived the following vapour-pressure formula for caesium:

$$\log p \text{ (bar)} = 10.65 - \frac{3992}{T},$$

where  $p$  is again expressed in bars. If  $p$  is expressed in mm. of mercury, the formula becomes

$$\log p \text{ (mm. Hg)} = 7.53 - \frac{3992}{T}.$$

If one compares the vapour pressures found in this manner with those obtained in other ways, one is immediately struck by the fact that the absolute values are very different. The absolute value for the vapour pressure of caesium is best given by the measurements of Kröner† which led to the following formula‡ for solid caesium (i.e. below the melting point):

$$\log p \text{ (mm. Hg)} = 7.53 - \frac{4075}{T}.$$

The values obtained from the formula of Langmuir and Kingdon are almost twice as great as those obtained from Kröner's formula. Rowe§ attempted to explain this by

\* I. Langmuir and K. H. Kingdon, *Proc. roy. Soc. A*, **107**, 76 (1925).

† A. Kröner, *Ann. Phys.*, Lpz., (4), **40**, 438 (1913).

‡ J. H. de Boer and C. J. Dippel, *Z. phys. Chem. B*, **21**, 273 (1933).

§ H. Rowe, *Phil. Mag.* **3**, 544 (1927).



assuming that the positive caesium ions do not have a single but a double charge, so that in the formula for the calculation of the vapour pressure from the positive-ion current  $\epsilon$  should be replaced by  $2\epsilon$ . This is highly improbable as the work of ionization for a second electron from  $\text{Cs}^+$  is 23.4 electron volts (Table II, § 11), a value much higher than the electron affinity of tungsten, making it impossible for a second electron to be removed from the caesium. Neither can the discrepancy be explained as due to the roughness of the tungsten filament, as was mistakenly assumed by the author.\* The surface of the tungsten filament may not, to be sure, be considered smooth, as we shall see in § 24. However, the number of atoms which strike the filament will not thereby be increased, and thus neither will the positive-ion current  $i$  be increased.

In order to explain the discrepancy one might imagine an apparent increase of the positive-ion current by the freeing of electrons from the caesium-covered plate which surrounds the filament, due to the bombardment with positive ions (§ 1). From this cause, however, a rise of 5 per cent. at the most could be expected.† An apparent increase of the positive-ion current might also be caused by the photoelectric freeing of electrons from the surrounding cathode due to illumination from the glowing tungsten filament. Measurements by Becker,‡ Ives,§ and very recently also by Taylor and Langmuir,|| actually show that at temperatures of the tungsten filament above  $1400^\circ\text{K}$ . this photoemission begins to play a part. In the measurements of Langmuir and Kingdon, however, the photoelectrons were of little importance. More important is the fact that the temperature of the surrounding caesium-covered cylinder is not exactly the same as that at the walls of the tube, but somewhat higher, due to the radiation from the tungsten filament. The vapour pressure of the caesium around the filament is thus somewhat higher than

\* J. H. de Boer and C. J. Dippel, *Z. phys. Chem. B*, **21**, 277 (1933).

† Estimated from the values for  $\text{Ne}^+$  on Fe, F. M. Penning, *Proc. Acad. Sci. Amst.* **31**, 14 (1928).

‡ J. A. Becker, *Phys. Rev.* **28**, 341 (1926).

§ H. E. Ives, *J. Franklin Inst.* **201**, 47 (1926).

|| J. B. Taylor and I. Langmuir, *Phys. Rev.* **44**, 445 (1933).

was to be expected, so that the difference between the determination of the vapour pressure by Kröner and that by Langmuir and Kingdon may be explained by this circumstance.

In their later work Taylor and Langmuir took the precaution of making the surrounding cylinder in the form of a layer of platinum deposited directly on the glass wall of the tube.\* This makes their measurements of the quantity of caesium atoms striking the filament per unit of time more trustworthy than the earlier vapour-pressure measurements, which is very favourable for their determinations of the fraction of the tungsten filament covered with the adsorbed caesium layer (§ 24). Becker always worked with unsaturated caesium vapour in his experiments, so that his determinations of the fraction of the surface occupied by the adsorbed layer are correct with respect to this point.

It must still be noted that at low temperatures of the tube walls ( $< 60^\circ \text{C.}$ ) and with saturated caesium vapour, there is a possibility that molecular ions  $\text{Cs}_2^+$  leave the filament, and not exclusively  $\text{Cs}^+$  ions.† Such behaviour would give rise to too low an estimation of the vapour pressure. By his use of unsaturated vapour Becker has no trouble with this possibility.

#### § 24. The determination of the fraction $\theta$ of the tungsten surface covered by the adsorbed caesium layer.

In their first articles Langmuir and Kingdon assumed a linear relation between  $\theta$ , the fraction of the tungsten surface covered with caesium, and the lowering of the work function. This means that it was assumed that every caesium ion or atom, independent of  $\theta$ , would contribute by the same amount to the electrical double layer, in other words, that every caesium atom or ion would create a constant dipole moment. As we know, in that case (see § 18)

$$\Delta V = 4\pi\sigma\mu,$$

or if, instead of the number of atoms per  $\text{cm.}^2$   $\sigma$ , we set  $\theta\sigma_0$ , where  $\sigma_0$  is the number of atoms per  $\text{cm.}^2$  that are adsorbed

\* J. B. Taylor and I. Langmuir, *Phys. Rev.* **44**, 429 (1933).

† Cf. H. E. Ives, *J. Franklin Inst.* **201**, 47 (1926).

when a fully occupied, monatomic layer is present, and  $\theta = \frac{\sigma}{\sigma_0}$ , the fraction of the surface that is covered, then

$$\Delta V = 4\pi\theta\sigma_0\mu.$$

It appeared later that as the fraction of the surface covered with caesium was increased, the work function did not decrease continually, but reached a minimum and thereafter increased again slightly. It was assumed that when the tungsten filament was covered with a monatomic layer, i.e. when  $\theta = 1$ , the work function was just at this minimum. We shall see more particularly in the treatment of the photoelectric properties of these layers (§ 41) that the photoelectric red threshold is shifted continually toward the longer wave-lengths with increasing value of  $\theta$  until it reaches a maximum wave-length, then returns somewhat, and finally becomes constant. Since Langmuir had objections against accepting the existence of an adsorbed layer that was more than one atom thick, it was rather arbitrarily assumed that the minimum of the work function was reached when  $\theta = 0.90$ , after which, between  $\theta = 0.90$  and  $\theta = 1.00$ , the work function again increased and the electron emission was again decreased.

The first real method of determining  $\theta$  experimentally was originated by Becker.\* A tungsten filament, first freed of all caesium by heating it to high temperature, is exposed at a lower constant temperature to a constant supply of caesium atoms, while the filament is made negative with respect to an anode, in order to measure the current of the emitted electrons. During the building up of the adsorbed layer the work function decreases, at first linearly with the time, then less strongly, and at the same time the logarithm of the emission current increases first linearly with the time and then less strongly. Thereafter the current reaches a maximum and again decreases, the filament always being exposed to a constant supply of caesium atoms (Fig. 26, curve  $T_1$ ). At another temperature of the filament  $T_2 > T_1$ , the progress is quite analogous, but the emission is naturally greater, due to the higher

\* J. A. Becker, *Phys. Rev.* **28**, 341 (1926).

temperature. It must be noted that the maxima of the curves are reached after the same length of time  $t_m$ . This is true for all temperatures lower than  $T_3$  (about  $650^\circ$  K.), which means that at these temperatures every caesium atom that strikes the filament is adsorbed by the surface, either in the form of an ion or in the form of an atom. Thus practically not a single atom is reflected, and the evaporation *before* the maximum has been reached may be neglected. For higher temperatures (Fig. 26,  $T_4$ ), this is no longer the case; because of the evaporation the maximum is no longer reached.

When the vapour pressure of caesium  $p_{\text{Cs}}$  is increased, i.e. when the supply of caesium atoms is increased, the time  $t_m$  becomes shorter, so that the product  $p_{\text{Cs}} \times t_m$  always remains constant. This means that the maxima of all the curves, independent of filament temperature or vapour pressure of caesium, occur when a very definite fraction of the surface is covered with adsorbed caesium. By measuring

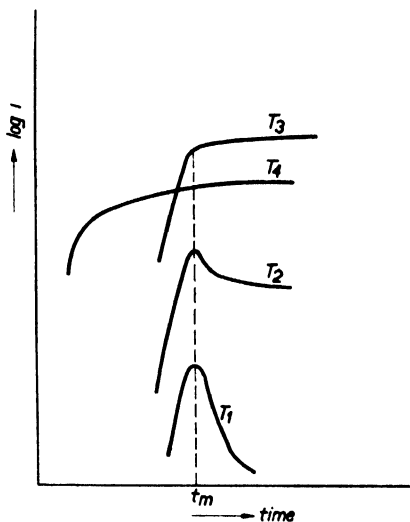


Fig. 26. Times of activation of [W]-Cs filaments, according to Becker, *Phys. Rev.* 28, 341 (1926).

ing the positive-ion current in the same manner as was described in the previous section, Becker was able to determine the number of atoms which struck the filament in unit time. If one multiplies this number by the corresponding value of  $t_m$ , and divides by the surface of the tungsten filament, then one finds  $\sigma_m$ , the number of caesium atoms per  $\text{cm}^2$  of the surface of the filament when the emission is at a maximum. Becker found

$$\sigma_m = 3.7 \times 10^{14} \text{ atoms/cm}^2$$

Since this number corresponds approximately with the number of caesium atoms which can be present when there is a monatomic layer on the tungsten filament, which number, as we

shall see later, is equal to  $3.56 \times 10^{14}$  atoms/cm.<sup>2</sup>, Becker concluded that the maximum emission and thus the minimum work function are reached when the surface is just covered by a monatomic layer, while thereafter, on adsorption of more caesium, a second adsorbed layer is added to the first, thus increasing the work function again. We shall see, however, that Becker has not taken into account sufficiently the increase in size which the surface of the tungsten filament undergoes by etching (by evaporation in the first process of cleaning the filament).

If the filament is now heated to a higher temperature in unsaturated caesium vapour, under which circumstance the filament is in dynamic equilibrium with the vapour and is only partially covered with caesium, one can easily measure  $\theta$ , the fraction of the surface covered with caesium, by cooling the filament suddenly to a temperature of about 550° K. and measuring the time necessary to reach the maximum emission. This time  $t_1$  is shorter than  $t_m$ , and the following relation holds:

$$\theta = 1 - \frac{t_1}{t_m}.$$

Since at the maximum of emission,  $\theta$  is not equal to 1, but as we shall see  $\theta = 0.67$ , all the values of  $\theta$  determined by Becker in this manner must be multiplied by 0.67.

Taylor and Langmuir\* later developed two other methods for the determination of  $\theta$ . The first of their methods is based on the fact that at small values of  $\theta$  all the atoms evaporate in the form of ions when the filament is suddenly flashed in an accelerating field at a high temperature. This method is thus valid for values of  $\theta$  for which the work function is still higher than the work of ionization of the caesium atom. The ion current is measured ballistically with a galvanometer and  $\theta$  can be calculated when the area of the surface of the filament is known.

Their second method is especially applicable in cases of higher values of  $\theta$ . In this method also the filament  $A$  is suddenly heated, but in a field such that no positive ions can

\* J. B. Taylor and I. Langmuir, *Phys. Rev.* **44**, 423 (1933).

escape. All the caesium atoms and ions present must therefore evaporate as atoms. A definite portion of this swarm of atoms is intercepted by a second filament *B*, which runs parallel with the first. Since the second filament *B* is positive with respect to the surrounding cylinders for the reception of ions, and is heated to glowing at a high temperature, all atoms intercepted by the filament *B* are transformed into ions which can again be measured ballistically with a galvanometer. Since in this method a second filament is used to measure the concentration on the filament *A* it is called "the two-filament method".

Filament *A* in the two-filament method was exposed to the vapour at a constant, low vapour pressure of caesium, and at a relatively low temperature until the adsorption equilibrium had been reached. Then in the above-described manner the quantity of caesium on *A* was determined. In a following experiment a lower temperature for *A* was chosen, and the quantity of caesium was again determined, and, as was to be expected, was found greater. At continually lower temperatures of the filament *A* the amount of adsorbed caesium increased, at first rapidly, and then more slowly, until finally at a definite temperature ( $\sim 325^\circ$  K. in the experiments of Taylor and Langmuir) it no longer increased. Only when the filament temperature was chosen very much lower, so that it was comparable with the temperature of the caesium reservoir, could an increase in the amount of adsorbed caesium again be observed. Thus the amount adsorbed remained constant over a relatively large temperature interval. This constant value is considered to correspond to a monatomic layer. The value found is equal to  $4.80 \times 10^{14}$  atoms/cm.<sup>2</sup>, where the filament is assumed to be smooth and round, and no account is taken of the true surface.

A tungsten filament which is etched during ageing by heating it to  $2900^\circ$  K. develops dodecahedral crystal faces\* on which there are  $1.425 \times 10^{15}$  tungsten atoms per cm.<sup>2</sup> As it appears from the crystal structure of caesium and tungsten that both metals have the same type of lattice (body-centred cubic), and as the radius of a caesium atom ( $2.68 \text{ \AA.}$ ) is almost double

\* I. Langmuir, *Phys. Rev.* **22**, 374 (1923).

that of the tungsten atom ( $1.37 \text{ \AA.}$ ), it may be assumed that in a monatomic adsorbed layer there will be one caesium atom per four tungsten atoms of the tungsten surface, so that

$$\frac{1.425 \times 10^{15}}{4} = 3.56 \times 10^{14} \text{ atoms/cm.}^2$$

can be adsorbed.

Since it was found above that  $4.80 \times 10^{14}$  atoms/cm.<sup>2</sup> of apparent surface were adsorbed in a monatomic layer, the true surface must be  $\frac{4.80}{3.56} = 1.35$  times the apparent surface.

If in the above-described experiments of Becker the filament was etched to the same amount, then the actual number of caesium atoms at maximum emission would have been  $\sim 2.7 \times 10^{14}$  atoms/cm.<sup>2</sup>, so that maximum emission would occur at  $\theta = \sim 0.75$ . As we shall see later (§ 28), Taylor and Langmuir found the optimum when  $\theta = 0.67$ . From these facts it may be concluded that in Becker's experiments the true surface of the tungsten filament was  $\frac{1}{0.67} = 1.5$  times the apparent.

## § 25. The evaporation of caesium atoms and ions as a function of $\theta$ .

As we saw in the previous section, Becker was able to determine  $\theta$  at a given temperature and at a given vapour pressure of caesium, by suddenly cooling the filament to  $550^\circ \text{ K.}$ , measuring the electron emission and ascertaining how much time was needed to reach the maximum of the emission. By making such determinations at different filament temperatures, and at a constant caesium vapour pressure, the relation between  $\theta$  and  $T$  is obtained, as is represented in Fig. 27 by the line  $ABC$ . If similar curves are made at various vapour pressures of caesium, it is possible to determine not only  $\theta$  as a function of the vapour pressure of caesium, i.e. the adsorption isotherm, but also the dependence on temperature of the equilibrium pressure of adsorbed caesium when  $\theta$  is constant.

The line  $ABC$  can only be obtained when during the experiment the filament is negative with respect to the surrounding cylinder ( $-140$  volts), in order that no positive caesium ions may escape. The dynamic equilibrium is thus given by the number of caesium atoms evaporating from the filament in unit time, and the number striking the filament out of the vapour. Consequently the adsorption isotherms obtained from such curves give the rate of evaporation of caesium atoms per cm.<sup>2</sup> per second ( $E_a$ ) as a function of  $\theta$ . Several such curves for various temperatures are given in Fig. 28. From these curves it can be seen that the quantity of caesium atoms evaporating

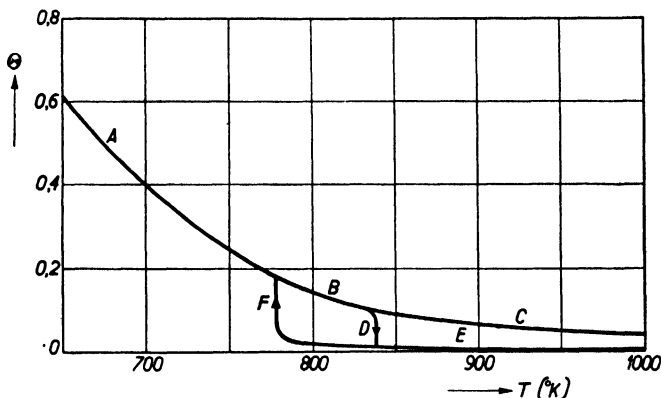


Fig. 27.  $\theta$  as a function of filament temperature, when atoms ( $ABC$ ) or ions ( $ADE$ ) are drawn from the filament. Figure according to Becker;  $\theta$  values corrected.

from unit surface in unit time at constant temperature increases strongly with increasing value of  $\theta$ .

If, however, one allows the adsorption equilibrium to be established while the tungsten filament is positive with respect to the surrounding cylinder, so that positive caesium ions may escape, one obtains for smaller values of  $\theta$  a different picture, represented by the line  $ABDE$  in Fig. 27. This is true when the adsorption equilibrium is established by starting from greater values of  $\theta$ . On the other hand, if one starts from a clean surface, then the filament remains practically clean at  $800^{\circ}$  K., and a higher value of  $\theta$  is only reached suddenly at lower temperatures (line  $EF A$  in Fig. 27). There is, however,



room for doubt as to whether this last line represents states of equilibrium (see also § 29).

During the establishment of the equilibria which lead to curves similar to  $ABDE$  in Fig. 27, the positive-ion current can be measured, so that the rate of evaporation of caesium ions per  $\text{cm}^2$  per sec. ( $E_i$ ) can be determined directly as a function of  $\theta$  at constant temperature. Hereby curves are obtained similar to those in Fig. 29. When the fraction of the surface covered is increased the positive-ion current increases

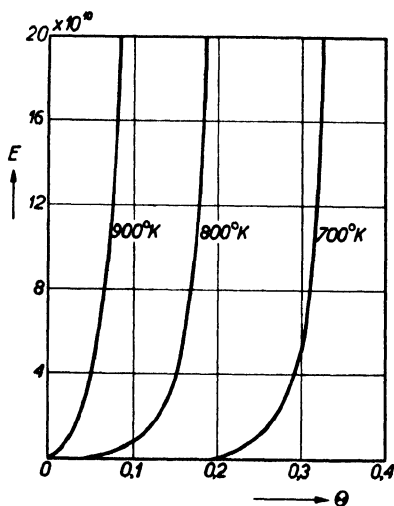


Fig. 28. Rate of evaporation of Cs atoms per  $\text{cm}^2$  per sec.,  $E_a$ , from a tungsten filament as a function of  $\theta$ .

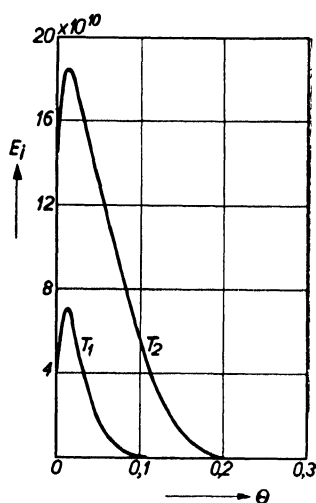


Fig. 29. Rate of evaporation of Cs ions from a tungsten filament at about  $800^\circ\text{K}$ .;  $T_2 > T_1$ .

at first linearly. A maximum is reached when the fraction of the surface covered is still quite small. Then the rate of evaporation of positive caesium ions decreases rapidly once more.

If one draws straight lines in Figs. 27 and 29 parallel to the  $E$  axis, one obtains the rate of evaporation as a function of the temperature at constant values of  $\theta$ . These functions can usually be expressed by the formula

$$\log E_{(a, \text{ or } i)} = a - \frac{b}{T},$$

where  $b$  is a measure of the heat of evaporation of the atoms or ions. For  $\frac{b}{T}$  one may use

$$\frac{b}{T} = \frac{L}{2.303RT} = \frac{L}{4.57T},$$

where  $L$  is the desired heat of evaporation in calories per gram molecule,  $R$  the gas constant (1.98 cal./mol.), and 2.303 is the conversion factor for converting natural into common logarithms. From Becker's\* measurement the following important conclusion could be made, that *the heat of evaporation of atoms decreases with increasing  $\theta$  while the heat of evaporation of ions increases with increasing  $\theta$ .*

Recent research by Taylor and Langmuir† has confirmed this behaviour. At the same time they found that in the evaporation of atoms, between the values  $\theta = 0.60$  and  $\theta = 0.06$ , the value of  $b$  can be represented by the empirical relation

$$b = \frac{32.380}{1 + 0.714\theta}.$$

For values of  $\theta$  less than 0.06 the value of  $b$  increases more than the formula represents, which means that the heat of evaporation increases by an extra amount. In Langmuir's‡ conception of such adsorption, where the decrease in the heat of evaporation of the atoms is brought about exclusively by repulsive forces between the adsorbed ions, which should begin to be inappreciable at small  $\theta$  values below  $\theta = 0.06$ , one should actually expect the value of  $b$  to be constant just in this region. The fact that this does not appear to be the case is explained by Taylor and Langmuir by the assumption that the surface of the tungsten is not really completely homogeneous, but that some active spots hold the atoms bound with more than the usual energy. They calculate that if 0.5 per cent. of the tungsten surface consists of such active areas, the adsorption by the rest of the surface can be represented by the normal formula. We shall see later, however, that for small values of  $\theta$

\* J. A. Becker, *Phys. Rev.* **28**, 357 (1926).

† J. B. Taylor and I. Langmuir, *Phys. Rev.* **44**, 432 (1933).

‡ I. Langmuir, *J. Amer. chem. Soc.* **54**, 2798 (1932).

the heat of evaporation of the adsorbed ions in the form of atoms must increase strongly with decreasing  $\theta$ , so that we should prefer not to introduce needlessly active spots, and we shall make use of the actual values derived from the figure of Taylor and Langmuir (see § 27).

**§ 26. Langmuir's conception of the nature of an adsorbed layer of caesium on tungsten.**

Before we begin to discuss our own views on the nature of the adsorption of caesium on tungsten, we shall first consider Langmuir's\* conceptions. He considers a single caesium atom adsorbed on a tungsten surface as an ion which is bound to the metal by means of its image force. The ion and its mirror image form a dipole which has its positive end directed away from the surface, and its axis perpendicular to the surface. Between two such dipoles on the surface, when one takes into account as Langmuir does only the component of the force parallel to the surface, there is a repulsive force which has the magnitude

$$f = \frac{3}{2} \frac{\mu^2}{r^4},$$

where  $\mu$  is the dipole moment, and  $r$  is the distance between the dipoles. Just as an equation of state is valid for the molecules in three-dimensional space like that of van der Waals'

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

where  $p$  represents the pressure,  $v$  the volume,  $T$  the temperature,  $R$  the gas constant and  $a$  and  $b$  are constants, and where  $\frac{a}{v^2}$  is connected with the attractive forces between the molecules, and  $b$  with the actual volume of the molecules themselves, similarly there will be such an equation for the adsorbed state

$$\left(F - \frac{a}{A_0^2}\right)(A_0 - A_0') = RT.$$

In this equation  $F$  is the spreading force of the adsorbed film (dynes/cm.),  $A_0$  is the area which contains a gram atom, and

\* I. Langmuir, *J. Amer. chem. Soc.* **54**, 2798 (1932); Nobel Lecture, *Angew. Chem.* **46**, 728 (1933); *Chem. Rev.* **13**, 147 (1933).

$A_0'$  the area which is actually occupied by adsorbed atoms.

The negative sign before the quantity  $\frac{a}{A_0^2}$  indicates that the forces are repulsive. If we let  $\sigma$  stand for the number of adsorbed atoms per unit area, then

$$\sigma = \frac{N}{A_0},$$

where  $N$  is Avogadro's number ( $6.06 \times 10^{23}$ ). Since  $R = kN$ , where  $k$  is the Boltzmann constant, the equation becomes

$$F = \frac{\sigma k T}{1 - \frac{\sigma}{\sigma_1}} + a' \sigma^2.$$

Langmuir then found that in the case of ions adsorbed on a metal surface which give rise to dipoles, the equation could be written

$$F = \frac{\sigma k T}{1 - \frac{\sigma}{\sigma_1}} + 3.34 \sigma^{\frac{1}{2}} \mu^2 + 1.53 \times 10^{-5} \sigma^2 T^{\frac{1}{2}} \mu^{\frac{1}{2}} c_i,$$

where  $c_i$  is a constant of integration whose value varies from 0.89 when  $\theta = 0$  to 0.05 when  $\theta = 0.9$ .

The spreading force  $F$  can also be represented as a function of  $E_a$ , the rate of evaporation, by means of Gibbs' adsorption equation

$$\frac{dF}{d \ln E_a} = \sigma k T.$$

In this manner the value of  $F$  can be calculated from the known values of  $E_a$  (see § 25), and from the values of  $F$  the dipole moment  $\mu$  can be calculated. The following values were found:

$$\begin{aligned} \mu &= 16.16 \times 10^{-18} \text{ e.s.u. when } \theta = 0, \\ \mu &= 8.28 \times 10^{-18} \text{ e.s.u. when } \theta = 0.50, \\ \mu &= 6.06 \times 10^{-18} \text{ e.s.u. when } \theta = 0.90. \end{aligned}$$

The work function is lowered by the layer of dipoles by an amount (see §§ 18 and 24)

$$\Delta V = 4\pi\theta\sigma_0\mu.$$

But since the electrons are influenced by the forces of the dipole layer only after they have left the surface, and have

already covered half the distance between the positive and negative poles, according to Langmuir only half of this quantity is put into force, so that the lowering of the work function can be represented by  $\Delta\phi = 2\pi\theta\sigma_0\mu$ .

By substituting the above-found values of  $\mu$ , and the corresponding values of  $\theta$ ,  $\Delta\phi$  can be calculated as a function of  $\theta$ .  $\Delta\phi$  can also be determined from the electron emission. The emission of pure tungsten can be given by

$$i_W = AT^2 e^{-\frac{\epsilon\phi_0}{kT}},$$

while that of a tungsten filament covered with caesium, as a function of  $\theta$ , can be given by

$$i_\theta = AT^2 e^{-\frac{\epsilon(\phi_0 - \Delta\phi_\theta)}{kT}}.$$

From this it follows that

$$\frac{i_\theta}{i_W} = e^{\frac{\epsilon\Delta\phi}{kT}},$$

so that  $\Delta\phi$  can be determined directly, if with Langmuir we let the values of  $A$  be the same for both cases. In order to determine  $\Delta\phi$ , the emission currents must be determined as they would be in the absence of any electric field. We have already seen that the emission is increased by an electric field (§ 9), and this increase seems to be much greater for cathodes covered with caesium than for pure metal cathodes. Taylor and Langmuir determine this emission for zero field graphically, from a curve which gives  $\log i$  as a function of the applied tension, and obtain finally values of  $\Delta\phi$  which agree excellently with those calculated from the evaporation of the atoms, up to  $\theta \leq 0.45$ , while the points measured extend only to values of  $\theta$  as low as  $\theta = 0.15$ . In the region from  $\theta = 0.10$  to  $\theta = 0.15$ , they calculate the values of  $\Delta\phi$  from the evaporation of positive ions, and obtain values which again agree excellently with those calculated from the evaporation of atoms.

In spite of the excellent agreement there are still several difficulties which must be noted. In the calculation of the values of  $\Delta\phi$  from the electron emission, it is quite incorrect to assume that the value of the constant  $A$  is the same in both

emission formulae, i.e. in that for  $i_w$  as well as in that for  $i_\theta$ . In § 38 we shall see that these values are different, and that the difference is quite important. Further, the substitution of 2 instead of 4 in the calculation of  $\Delta\phi$  from  $\theta$  and  $\mu$  is only permissible when the virtual part of the dipole, existing in the metal, is really as great as the actual part of the dipole in the adsorbed ions. In the picture which Langmuir created of mutually repulsive dipoles, which, by this repulsion, reduce each other in magnitude, this is not the case. For the rest, the whole conception of the process of formation of the magnitude of the moment of this dipole is not acceptable.\*

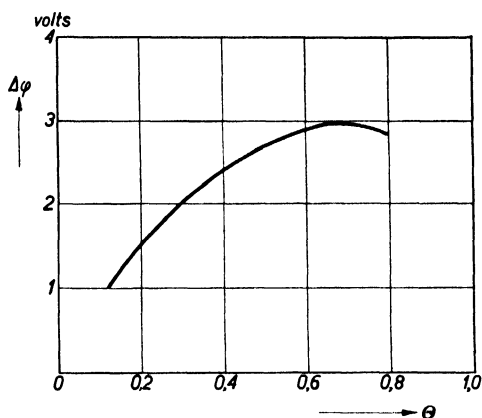


Fig. 30.  $\Delta\phi$  (Cs on W) as a function of  $\theta$ , according to J. B. Taylor and I. Langmuir.

Fig. 30 gives the values of Taylor and Langmuir for  $\Delta\phi$  as a function of  $\theta$  determined from the emission. This  $\Delta\phi$  represents at the same time the contact potential (§ 10) between a tungsten filament covered with caesium and a clean tungsten filament.

It can be seen that  $\Delta\phi$  is at a maximum when  $\theta = 0.67$ , and that it then decreases again (§ 24). Langmuir explains this decrease by the assumption that the caesium atoms in the adsorbed layer approach each other more closely, whereby, as is always the case when the distance between atoms is reduced, the work function increases. This explanation is, however,

\* J. H. de Boer and C. F. Veenemans, *Physica*, 1, 953 (1934).

rather forced, and we shall see in § 28 that the decrease in  $\Delta\phi$ , or the increase in work function after the maximum (minimum of the work function), is caused by the presence of dipoles with their negative ends toward the outside among the other dipoles.

§ 27. The adsorption of ions, and the lowering of  $\phi_0$  at small values of  $\theta$ .

We shall now continue with our treatment of the adsorption of caesium on tungsten at small values of  $\theta$  (Chap. II, § 20). For this purpose we must again make use of the potential

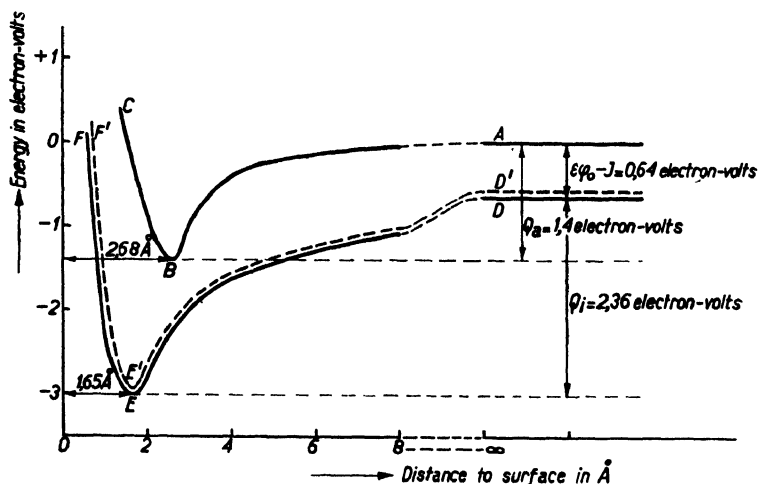


Fig. 31. Potential curves, relating to the adsorption of caesium atoms and ions on a tungsten surface.

curves which were treated in detail in Chap. II. If when a caesium atom was adsorbed on a tungsten surface we could prevent its ionization, then, leaving out of account the energy at absolute zero, the equilibrium position of the atom with respect to the tungsten surface would be given by the minimum  $B$  of the potential curve  $ABC$  in Fig. 31. At point  $B$  the distance to the metal surface is practically equal to the radius of the caesium atom, or  $2.68 \text{ \AA}$ . The adsorption energy of an isolated atom cannot be determined experimentally; we shall see that all the energies of evaporation of adsorbed caesium as atoms found experimentally relate to other quantities. It is

also impossible to calculate this energy theoretically, because of the lack of data. According to a known rule, however, the adsorption energy is approximately equal to half the geometric average of the heats of evaporation of the components.\* So we may write

$$Q_a \sim \frac{1}{2} \sqrt{L_{Cs} L_W},$$

where  $Q_a$  is the required adsorption energy and  $L_{Cs}$  and  $L_W$  represent the heats of evaporation. In this manner  $Q_a$  is found to be about  $\frac{1}{2} \sqrt{0.81 \times 9.6} \cong 1.4$  electron volts.

However, the caesium atom is ionized when it reaches the neighbourhood of the tungsten filament, and the electron is taken up by the filament. In this process, for which no adsorption is necessary as it may occur before the atom comes into contact with the tungsten filament, the energy  $\epsilon\phi_0 - I = 4.52 - 3.88 = 0.64$  electron volt is gained. The caesium ion polarizes the tungsten metal so that the force can always be described as the action of the mirror image of the ion (§§ 8 and 19). The energy of combination due to this attraction

is equal to  $\frac{\epsilon^2}{4r_i}$ , where  $r_i$  is the distance of the caesium atom

from the surface. This distance can again be set equal to the radius of the caesium ion,† so that  $r_i = 1.65 \text{ \AA.}$ , and the energy of combination due to the attraction by the image force is found to be

$$Q_{im} = 2.17 \text{ electron volts.}$$

There are other forces present besides this image force. The polarization of the caesium ion by the induced negative charge gives a very small contribution, and in addition the ion is attracted by means of the van der Waals force (§ 16). There are also repulsive forces which diminish the energy again. By taking into account all these other forces the final value for  $Q_i$  was obtained as  $Q_i = \sim 2.3$  electron volts.†

If one now evaporates the adsorbed caesium in the form of atoms, as was described in § 25, by giving the surrounding cylinder a positive tension to prevent the escape of positive

\* A. Eucken, *Z. Elektrochem.* **28**, 11 (1912); *Lehrbuch der chemischen Physik*, pp. 455, 483, Leipzig (1930); J. H. de Boer and J. F. H. Custers, *Z. phys. Chem. B*, **25**, 225 (1934).

† J. H. de Boer and C. F. Veenemans, *Physica*, **1**, 753 (1934).



ions from the filament, then one must supply as energy of evaporation the energy equivalent to the difference in level between the points  $E$  and  $A$ , or

$$L_a = Q_i + \epsilon\phi_0 - I = \sim 2.3 + 4.52 - 3.88 = \sim 2.95 \text{ electron volts.}$$

The experimental determination of the heat of evaporation in the form of atoms by Taylor and Langmuir shows (when we use the actual values found by them, as was noted in § 25, and take no account of the "active spots") that  $L_a$  for a clean tungsten filament, i.e. when  $\theta = 0$ , has the value of 3.0 electron volts. The experiment thus confirms the value of our derived result, and we may accept the value 2.36 electron volts for  $Q_i$ .

When more atoms arrive at the filament and are adsorbed as ions, we must take account of the fact that the gain in energy from the ionization is smaller for each atom than for the preceding atom. This is due to the fact that the work function  $\phi_0$  is lowered by means of the positive-ion adsorption by an ever-increasing amount  $\Delta\phi_\theta$ . Thus whenever there are already some positive ions adsorbed, the starting level  $D'$  of the ionic adsorption curve, as well as its minimum  $E'$ , must be higher by an amount  $\epsilon\Delta\phi_\theta$  than  $D$  and  $E$ . Since at the beginning of the building up of the adsorbed layer, when  $\theta$  is *small*, the lowering of  $\phi$ ,  $\Delta\phi_\theta$  is *certainly proportional* to the number of adsorbed ions, the heat of evaporation in atomic form (difference in height between  $E'$  and  $A$ ) decreases proportionally with  $\theta$ , whereby the rate of evaporation in atomic form increases exponentially. According to the equation

$$\log E_a = a - \frac{b}{T},$$

the logarithm of the rate of evaporation  $E_a$  changes (see § 25) linearly with  $b$ , thus with the heat of evaporation. This rapid increase of  $E_a$  with  $\theta$  (Fig. 28) is just what Becker observed experimentally, and also what Taylor and Langmuir found. We see thus that the heat of evaporation of the adsorbed caesium decreases with increasing  $\theta$ , not because there are at first active spots which later disappear, nor because the dipoles repulse each other, but because there is continually less energy needed to obtain the necessary electrons for the evaporation

of the adsorbed ions in the form of atoms at greater values of  $\theta$ , due to the lowered work function.

If the adsorbed ions are allowed to evaporate in the form of ions, a smaller amount of energy  $Q_i$  is necessary. When a very small fraction of the surface is covered, the energy necessary for the ion evaporation remains  $Q_i$ , since there are no mutual influences among the ions on the surface. When, however, a larger fraction of the surface becomes covered, the bond of a new ion is influenced by the presence of a certain ion occupation, and the energy of combination is thereby *increased*. The

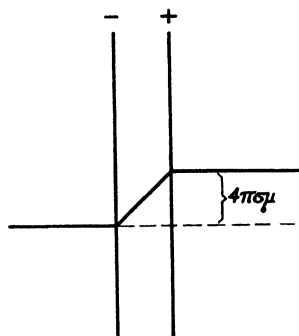


Fig. 32. Change of potential energy of a positive ion, passing through a double layer with homogeneously distributed electric charge.

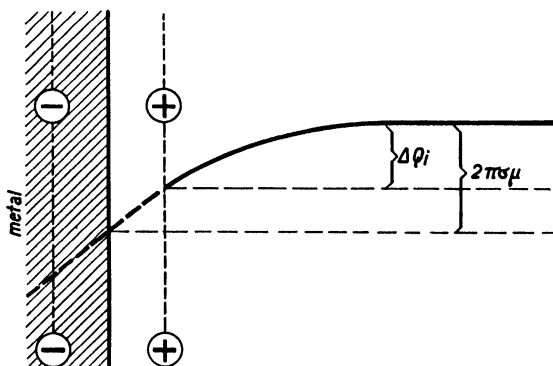


Fig. 33. A positive ion is bound by an extra amount of energy  $\Delta Q_i$ , when other positive ions are already present on the metal surface.

forces arising in the double layer already present are so directed that they attract a positive charge toward the surface. A double layer whose charges could be considered to be distributed homogeneously would not exert any such action, and in that case the progress of the potential would be as is given in Fig. 32. In this case, directly outside the double layer there is no longer any force which can attract ions. If, however, we take into account the atomic structure, we obtain a potential curve such as that already given in Fig. 23 of § 18. Fig. 33 shows the course of the potential for the case in which

a positive ion is added to the double layer at a point lying in the centre of four positive ions at the corners of a square on the surface. As is evident an amount of energy  $\Delta Q_i$  is gained which must be added to the above-mentioned adsorption energy  $Q_i$ . This  $\Delta Q_i$  begins to be appreciable when 1 per cent. of the surface is occupied, and increases linearly with  $\theta$  until more than 10 per cent. is occupied. Therefore the ionic evaporation will increase with increasing  $\theta$  from  $\theta=0$  to  $\theta=0.01$ , but with greater increase of  $\theta$  it will decrease exponentially with  $\theta$  because of the linear increase of the ionic heat of evaporation. This behaviour agrees completely with the experimental results\* (see Fig. 29 in § 25).

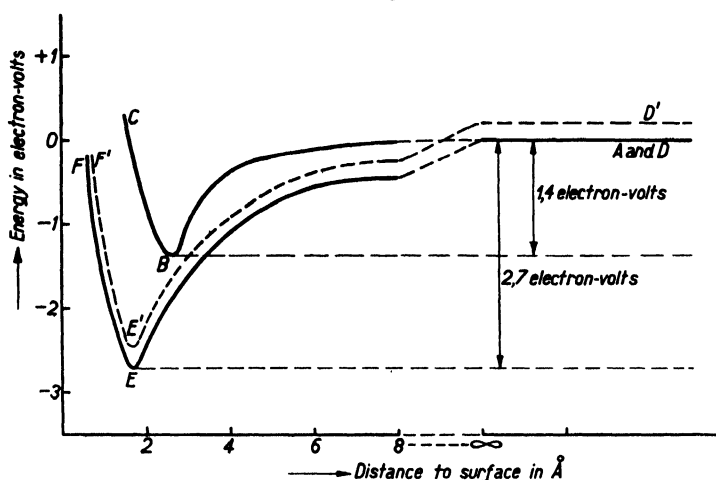


Fig. 34. Potential curves of Cs on W, when  $\theta=0.07$ .

As soon as the work function is decreased by 0.64 volt, due to the ever-increasing fraction of the surface covered with positive ions, the amount  $\epsilon(\phi_0 - \Delta\phi) - I$  is just equal to zero, and the heat of evaporation of the adsorbed ion must be the same for evaporation in the form of atom and in the form of ion, and must equal  $Q_i + (\Delta Q_i)_\theta$ . When still more caesium is adsorbed the caesium atoms will continue to be ionized during adsorption, since  $E'$  is still lower than  $B$ , but the majority will evaporate in the atomic form, since the difference in level between  $E'$  and  $A$  is less than that between  $E'$  and  $D'$  (see Fig. 34).

\* J. A. Becker, *Trans. Amer. Electrochem. Soc.* **55**, 169 (1929), formula 3.

Measurements by Taylor and Langmuir\* show that when up to 7 per cent. of the surface is occupied, upon sudden flashing of the filament, all the adsorbed ions evaporate as ions, and that when  $\theta > 0.07$ , even with an accelerating field, the evaporation as atom exceeds that as ion. It may thus be concluded that when  $\theta = 0.07$  the point is reached at which the work function has become just equal to  $I$ . In that case  $\Delta\phi = 0.64$  volt and the active dipole moment  $\mu$  may be calculated from the equation

$$\Delta\phi = 4\pi\sigma_0\theta\mu,$$

where by  $\mu$  is meant that part of the dipole moment which effectively acts to decrease  $\phi$ , i.e. which projects above the metal surface. When  $\mu$  is so defined we may continue to use the factor 4. Since  $\sigma_0 = 3.563 \times 10^{14}$  atoms per cm.<sup>2</sup> and  $\theta = 0.07$ , we obtain, by multiplying by 300 to convert volts into electrostatic units,

$$0.64 = 300 \times 4\pi \times 3.563 \times 10^{14} \times 0.07 \mu,$$

$$\mu = 6.8 \times 10^{-18} \text{ e.s.u.}$$

This latter value agrees very well with that which can be calculated by the use of our theory.† The acting portion of the dipole moment, which projects beyond the metal surface, is built up from the charge of the positive ions, which have their position at a distance from the metal equal to the radius of the caesium ion (1.65 Å.), and from the dipole moment  $\mu_a$  induced on the caesium ion by the negative charge of the mirror image (see Fig. 35). The total moment is thus

$$\mu = \epsilon r - \frac{\alpha\epsilon}{(2r)^2} = 7.85 - 1.08 = 6.75 \times 10^{-18} \text{ e.s.u.}$$

As a result of this good agreement, we may be permitted to state that in this region of the adsorption of ions every ion contributes practically the same amount to the double layer. As a matter of fact the dipole moment per ion must decrease slightly when larger fractions of the surface are covered, since the polarization of the caesium becomes slightly greater. This

\* J. B. Taylor and I. Langmuir, *Phys. Rev.* **44**, 428 (1933).

† J. H. de Boer and C. F. Veenemans, *Physica*, **1**, 953 (1934).

last fact arises from the same cause as does the increase in the ionic adsorption energy. But since this effect is of the second order it may easily be understood that there will be small chance of observing the decrease of the total dipole moment in the region of small values of  $\theta$ .

Langmuir and Kingdon's\* measurements relating to the electron emission are in complete agreement with the above picture. They found the following relation to be valid for very small fractions of the surface covered:

$$i \log \frac{i}{i_W} = C p_{Cs},$$

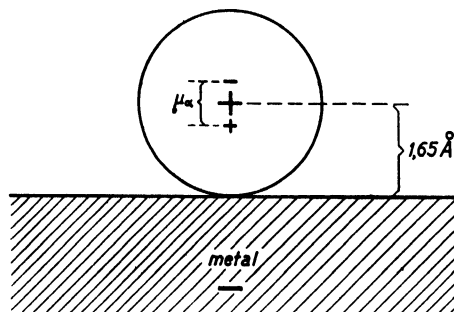


Fig. 35. The dipole of a Cs ion on a tungsten surface.

where  $i$  is the electron emission current of the caesium-covered tungsten filament at a definite, constant filament temperature,  $i_W$  is the emission current of a clean tungsten surface at the same temperature,  $p_{Cs}$  the vapour pressure of caesium at a given temperature of the tube, and  $C$  a constant. When small fractions of the surface were covered (a few per cent. only, as we now know) there occurred discrepancies in that  $i \log \frac{i}{i_W}$  increased more rapidly than was to be expected from the above relation.

This behaviour may be deduced from the picture here developed.† On the adsorption of a caesium atom as an ion on the surface, the energy  $\epsilon(\phi_0 - \Delta\phi_\theta) - I + Q_i$  is gained. If there are

\* I. Langmuir and K. H. Kingdon, *Proc. roy. Soc. A*, **107**, 71 (1925).

† J. H. de Boer and C. F. Veenemans, *Physica*, **1**, 957, 963 (1934).

$n$  caesium atoms per unit volume of vapour, the number of adsorbed ions  $\sigma$  will be proportional to the number  $n$  and to a power of  $e$ , in which the gain in energy occurs in the exponent

$$\sigma = ane^{\frac{\epsilon(\phi_0 - \Delta\phi_\theta) - I + Q_i}{kT}},$$

where  $a$  represents the proportionality factor. As  $Q_i$  is constant at very small degrees of occupation of the surface, and as  $I$  is of course always a constant, the above expression may be written as follows for a constant temperature  $T$ :

$$\sigma = bne^{\frac{\epsilon(\phi_0 - \Delta\phi_\theta)}{kT}},$$

where  $b$  is again a constant. The electron emission, as is already known, may be represented by the formula

$$i = A_\theta T^2 e^{\frac{-\epsilon(\phi_0 - \Delta\phi_\theta)}{kT}},$$

so 
$$e^{\frac{\epsilon(\phi_0 - \Delta\phi_\theta)}{kT}} = \frac{A_\theta T^2}{i}.$$

Dividing the emission formula by the emission for pure tungsten and taking the logarithm of the result we obtain

$$\log \frac{i}{i_W} = \log \frac{A_\theta}{A} + \frac{\epsilon \Delta\phi_\theta}{kT},$$

where  $i_W$  is the emission for pure tungsten at the temperature  $T$  and  $A$  corresponds to the  $A$  value in the emission formula for pure tungsten. As we have already mentioned in § 26  $A_\theta$  is not a constant, but is dependent on  $\theta$ . The dependence can be expressed by the following formula:\*

$$A_\theta = Ae^{-a\theta},$$

where  $a$  is a constant (see also § 49).  $\log \frac{A_\theta}{A}$  changes according to this formula linearly with  $\theta$ , and thus with  $\sigma$ , and since at the beginning when only ions are adsorbed  $\Delta\phi_\theta$  is also proportional to  $\sigma$ , we may write simply

$$\log \frac{i}{i_W} = B'\sigma \quad \text{or} \quad \sigma = B \log \frac{i}{i_W},$$

\* Cf. W. Schottky and H. Rothe, *Handbuch der Experimentalphysik*, 13, 2, p. 165 (1928).

in which  $B'$  and  $B$  are proportionality factors. The number  $n$  of caesium atoms in the vapour is proportional to the vapour pressure  $p_{\text{Cs}}$ ,

$$n = cp_{\text{Cs}},$$

so that finally

$$\begin{aligned} B \log \frac{i}{i_{\text{W}}} &= \sigma = bne^{\frac{\epsilon(\phi_0 - \Delta\phi_\theta)}{kT}} = bcp_{\text{Cs}} \times \frac{A_\theta T^2}{i} \\ &= bcp_{\text{Cs}} A T^2 e^{-a\theta} \times \frac{1}{i}, \end{aligned}$$

or, combining all the constants  $B$ ,  $b$ ,  $c$ ,  $A$  and  $T^2$  in the one constant  $C$ ,

$$\log \frac{i}{i_{\text{W}}} = Cp_{\text{Cs}} e^{-a\theta} \times \frac{1}{i}.$$

We have already seen that when slightly more than 1 per cent. of the surface is covered  $Q_i$  may no longer be considered constant, but increases with an amount  $\Delta Q_i$ . Therefore there must be a correction in the expression for  $\sigma$  and it becomes

$$\sigma = bne^{\frac{\epsilon(\phi_0 - \Delta\phi_\theta)}{kT}} \times e^{\frac{\Delta Q_i}{kT}},$$

so that the final equation becomes

$$i \log \frac{i}{i_{\text{W}}} = Cp_{\text{Cs}} \times e^{-a\theta} \times e^{\frac{\Delta Q_i}{kT}}.$$

When small fractions of the surface are covered both  $e$  powers are small, and since in addition they act against each other, it is quite plain why, in the beginning,  $i \log \frac{i}{i_{\text{W}}}$  is proportional to  $p_{\text{Cs}}$ . When larger fractions of the surface are covered (more than a few per cent.) the last  $e$  power becomes the more significant and  $i \log \frac{i}{i_{\text{W}}}$  increases more rapidly than  $p_{\text{Cs}}$ .

## § 28. The process of the adsorption of caesium and the electron emission at larger values of $\theta$ .

We have seen above (Fig. 34) that at the moment when the work function is lowered to such an extent that it is equal to the ionization potential  $I$  of caesium (coincidence of the levels  $A$  and  $D$ ), the minimum of the ionic adsorption curve  $E$  is still

much lower than that of the atomic adsorption curve  $B$ . At that moment the adsorption energy for an ion, as is indicated in the figure, is equal to 2.7 electron volts,\* and since the same energy for an atom is 1.4 electron volts, there is a difference of 1.3 electron volts.

One might now expect that the ion adsorption would continue, the level  $D$  being continually raised, until the minimum of the ionic adsorption curve  $E'$  were as high as  $B$ . Before this state is reached, however, atoms are already being adsorbed. When an atom is added on the tungsten surface beside and

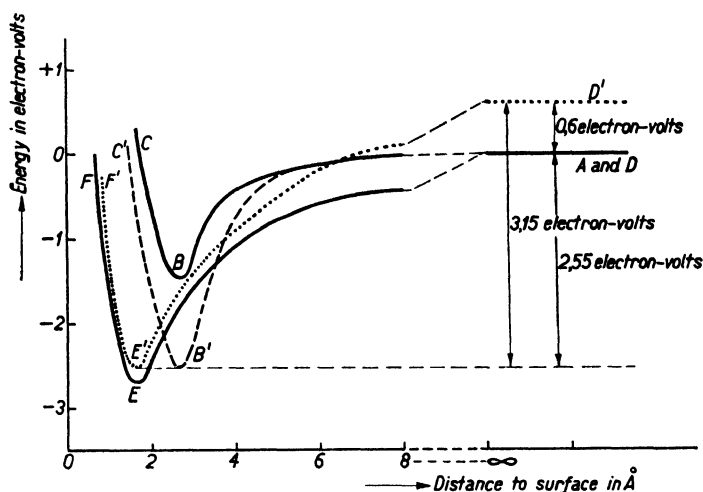


Fig. 36. Adsorption of atoms beside ions and end of ion adsorption.

directly in contact with a caesium ion already present, an extra amount of energy is gained over and above the above-mentioned 1.4 electron volts, due to the polarization of this atom by the ion. Let curve  $AB'C'$  (Fig. 36) represent the potential curve for this atom. Then we see that the ionic adsorption can continue until the minimum  $E'$  reaches the same height as the minimum  $B'$ . From this moment newly arriving caesium atoms are adsorbed as atoms in the position just described. Since in this position, due to the polarization, they also have a dipole (see Fig. 37) which is so directed that

\* J. H. de Boer and C. F. Veenemans, *Physica*, 1, 960 (1934); a second article will appear shortly in *Physica*, 2 (1935).



one component is vertical to the surface, and with the positive end directed away from the surface, these atoms will also contribute to a further decrease in the work function. By continued adsorption all the ions on the surface will have such polarized atoms next to them, until at the moment when every ion has collected four atoms about itself, the minimum in the lowering of  $\phi$  is reached. If now still more atoms are adsorbed they take up a position practically midway between the ions, since as we shall see directly the surface is already

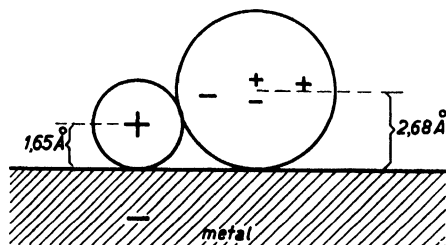


Fig. 37. Atom beside an ion on a metal surface.

about two-thirds occupied. Such atoms, however, which are bound by van der Waals' forces to the surface and to the caesium atoms already present (atom *A* in Fig. 38), are polarized in such a way that their (weak) dipoles are placed with their negative ends toward the outside. We saw in § 27 that the forces arising in the double layer were so directed that at these points

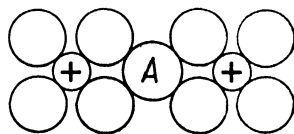


Fig. 38. Atom *A* is bound between the groups of atoms around the ions.

negative charges were repulsed and positive attracted. The same type of force which allows  $Q_i$  to increase by  $\Delta Q_i$  at small values of  $\theta$ , causes in this case an oppositely directed polarization of the newly arrived atoms.

The work function is thus slightly raised again after passing a minimum at the moment when each one of the ions has four atoms arranged about itself. Taylor and Langmuir decided on the basis of their measurements that this minimum was reached when  $\theta = 0.67$ . From this value it can be calculated that the maximum occupation of the surface by ions is  $\frac{67}{8} = 13.4$  per cent. By the use of the dipole moment  $6.8 \times 10^{-24}$

e.s.u., which was derived in § 27, it can be calculated that the lowering of the work function due to the ions only equals 1.22 volts. When at  $\theta = 0.134$  only ions are present and no atoms, the level  $D'$  (see Fig. 36) is 0.6 electron volt higher than the level  $A$ . In addition,  $Q_i$  has been raised to about 3.15 electron volts,\* and the adsorption energy of the first caesium atom which is added next to an ion on the surface is about 2.55 electron volts. During the building up of the adsorbed layer with atoms the heat of evaporation in atomic form decreases continually, since the adsorbed atoms repel each other by means of the dipoles which are suitably directed for that purpose. The energy of combination of the ions increases continually during this process. The increase in the energy of combination of the ions as well as the further decrease in the adsorption energy of the atoms is in agreement with the experiments of Becker, and of Taylor and Langmuir.

The whole adsorption process is briefly the following. The first atoms to arrive are adsorbed as ions, and thereby form a double layer which lowers the work function. By means of the forces originating in this double layer,  $Q_i$ , the combining energy of the ions continually increases. In the beginning the heat of evaporation as atom is greater than that as ion, but it decreases continually, because since the level  $E$  is increasing (Figs. 31, 34 and 36) the difference in level with  $A$  grows steadily less. When  $\theta = 0.07$  the energy of evaporation as atom (from the adsorbed ion) is equal to the combining energy of the ions, and when  $\theta$  is larger this energy of evaporation becomes smaller. The ionic adsorption continues, however, because the combining energy of the ions is always greater than the adsorption energy of the atoms multiplied by the value of  $I - e\phi_\theta$  which is valid at that moment. But when  $\theta = 0.134$  the adsorption energy of the atoms which are adsorbed next to ions on the surface is great enough to prevent further ionic adsorption. The atoms which are now added continue to lower the work function; the adsorption energy of the atoms decreases with increasing  $\theta$ , the combining energy

\* J. H. de Boer and C. F. Veenemans, will appear shortly in *Physica*, 2 (1935).

of the ions increases. From  $\theta = 0.67$  on, newly arriving atoms are polarized in such a way that the dipoles are directed in the opposite direction to that of the dipoles in the double layer; the work function now increases.

In the discussion of the photoelectric phenomena of these layers we shall see that the adsorbed atoms which lower the work function as well as those which raise it behave differently with respect to a temperature increase than the adsorbed ions. The process of ionic adsorption does not break off suddenly at  $\theta = 0.134$  and atomic adsorption then begin. On the contrary, even at smaller values of  $\theta$  atoms are adsorbed together with ions, until 13.4 per cent. of the surface is occupied by ions. There is a continual transition process: at small values of  $\theta$  only ions are adsorbed on the surface, at larger  $\theta$  values atoms are also adsorbed beside the ions, and then the adsorption of ions stops completely at still higher values of  $\theta$  and only atoms are adsorbed.

### § 29. Some features of the evaporation in the form of ions.

In § 25 (see Fig. 27) we saw that when a tungsten filament covered with caesium is heated to higher and higher temperatures while at the same time positive ions are drawn from the filament, at the point when about 7 per cent. of the surface is occupied the percentage of the surface occupied is suddenly reduced to a very small value. This behaviour is closely connected with the evaporation curves for ions and atoms which we met in § 25.\* In Fig. 39 the rates of evaporation  $E$  of ions as well as of atoms are again schematically given for several temperatures.  $T_2$  is a higher temperature

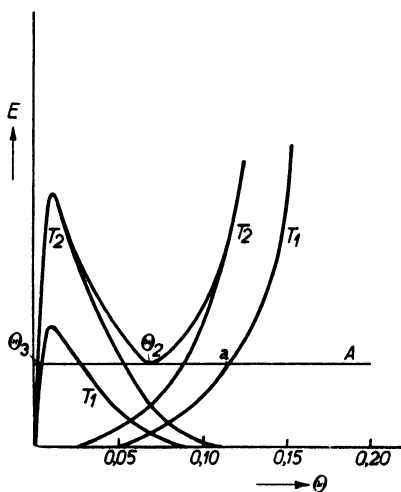


Fig. 39. Rates of evaporation of atoms and ions.  $T_2 > T_1$ .

\* J. A. Becker, *Phys. Rev.* **28**, 355 (1926); J. B. Taylor and I. Langmuir, *Phys. Rev.* **44**, 440 (1933).

than  $T_1$ . Let  $A$  be the number of atoms per unit time which strike the surface of a filament surrounded by caesium vapour per cm.<sup>2</sup> At the dynamic equilibrium for the temperature  $T_1$  of the filament, just as many atoms per unit of time strike the filament as evaporate from it. The degree of occupation is given by the value of the interception of the evaporation curve for temperature  $T_1$  and the line  $A$ , i.e. by the value of point  $a$ . If the filament temperature is now raised to  $T_1'$ ,  $E$  becomes higher than  $A$ , atoms are evaporated, and a new equilibrium is reached which is given by the interception of a new evaporation curve corresponding to the temperature  $T_1'$  with the line  $A$ . This curve lies slightly more to the left and a point is obtained to the left of  $a$  (smaller value of  $\theta$ ). If the temperature is now raised to  $T_2$  the figure shows that the total evaporation (as ion and as atom together) just touches the line  $A$ . Further increase of the temperature causes an increase in the rate of evaporation, especially of that as ion, which in turn causes a decrease in  $\theta$ . A decrease in  $\theta$  means here, however, that still more ions evaporate, since the energy of evaporation as ion decreases with decreasing  $\theta$ . The state has now become labile; the evaporation of ions begins suddenly at  $\theta_2$  and continues until the interception  $\theta_3$  is reached, where the system is again stable. This explains the sudden decrease of  $\theta$  upon increase of temperature as at point  $D$  in Fig. 27 of § 25. In this process the adsorbed ions evaporate suddenly as ions, as Becker observed. Further, it will be plain that this behaviour will not be observed for evaporation in a retarding field; then no ions evaporate, and upon increase of temperature in Fig. 39 we continue to move steadily toward the left along the interceptions with the atomic evaporation curves, obtaining the continuous curve  $ABC$  in Fig. 27.

When a tungsten filament is exposed to a constant supply of caesium atoms at a constant temperature  $T$ , the fraction of the surface covered increases proportionally with the time until the equilibrium value of  $\theta$  is reached, because every atom which strikes the surface is adsorbed (see also § 24). Line  $a$  in Fig. 40 represents this increase of  $\theta$  as a function of the time of exposure. When, however, during the exposure the filament

is positive with respect to a surrounding cylinder, then  $\theta$  increases at first only slightly, and only after some time, when some ions are already adsorbed, does the normal increase of  $\theta$  follow as indicated by line *b* in Fig. 40. Thus, when positive ions can be drawn from the filament only a very few of the atoms at first arriving on the filament are adsorbed. We must perhaps imagine here that the atoms are already ionized at some distance from the filament, whereby the filament takes up the electrons (filament is positive), but also that the positive ion is not yet close enough to the tungsten surface for the image attraction to exceed the forces arising from the applied electric field. Only after some ions are adsorbed on the filament is the attractive force for new ions increased by means of the field of the double layer, and moreover it is enabled to act over a greater distance, so that from then on all the ions are bound.

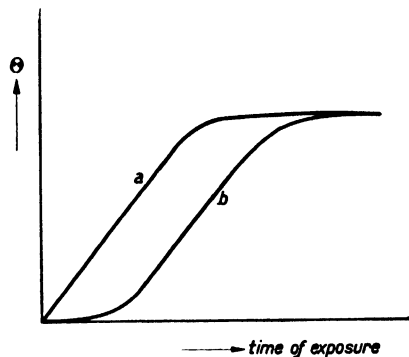


Fig. 40.  $\theta$  as a function of time of exposure: (a) with filament negative; (b) with filament positive.

Hysteresis phenomena which have been studied in detail by Becker are connected with the above-described phenomena, of which line *EF A* in Fig. 27, § 25, gives an example.

### § 30. A second layer adsorbed on the first monatomic layer.

According to Becker's conception a second layer is adsorbed over the first, when the maximum of the electron emission is passed. Taylor and Langmuir, however, concluded from their measurements that the maximum occurs at  $\theta = 0.67$ , and that during the ensuing decrease in the electron emission (increase of the work function) the monatomic layer is filled to completion, and that thereafter the adsorption stops except for temperatures of the filament nearly equal to that of the saturated caesium vapour. We see that this conception agrees in every respect with that developed in the foregoing sections.

Since up to a value  $\theta = 1$  practically all the caesium atoms which strike the filament remain adsorbed there must always be some combination of caesium atoms to form a second layer. When  $\theta$  is relatively large, very many atoms do not strike the surface exactly at a vacant spot, but at a spot where there are already atoms adsorbed. If these atoms were not temporarily bound, they would not be able to contribute to the further building up of the layer, to which, as we have seen, they as a matter of fact do contribute. The atoms added to the second (or even third) layer possess a large degree of mobility in that layer, so they are able to move quickly into the still vacant places in the underlying layer. Just as condensation takes place mainly via a second layer, in the same way evaporation also takes place, and for this evaporation also a high degree of mobility of the atoms within the layer is necessary.

When the temperature of the filament is kept low, and is only slightly higher than the temperature of the walls of the tube, which latter temperature controls the vapour pressure of the caesium, noticeable quantities of caesium are adsorbed in the second layer. This occurs only when the adsorbed caesium layer is in equilibrium with the nearly saturated vapour.

In the first caesium layer adsorbed directly on the tungsten surface, the adsorbed atoms (and ions) have, at least at sufficiently high temperatures, a large degree of mobility. Langmuir and Taylor\* found that ions which take up a quantity of 0.61 electron volt or more from the thermal energy can be torn out of their places, and take part in this surface migration. Much less energy must thus be supplied for this movement along the surface than for evaporation. That the measurements of Langmuir and Taylor were made when very small fractions of the surface were covered, indicates that the ions which normally occupy a very definite position on the surface with respect to the underlying tungsten lattice, must have an energy of 0.61 electron volt in order to move from the favourable position, via a position in which they are less strongly bound, into another favourable position. In § 36 we shall return to the subject of surface migration.

\* I. Langmuir and J. B. Taylor, *Phys. Rev.* **40**, 463 (1932).

## CHAPTER IV

### OTHER ELECTROPOSITIVE METALS ON METAL SURFACES

#### § 31. The adsorption of various alkali metals on tungsten and other metals.

The principle of the adsorption on tungsten of the other alkali metals, as well as of barium and even of thorium, is the same as that of caesium. In all cases the work function of the tungsten is very much lowered, and at small values of  $\theta$  this lowering is proportional to the quantity of adsorbed material. Thus in all these cases a dipole layer is formed on the surface with its positive side away from the surface, and it is reasonable to ascribe the formation of this layer to the adsorbed positive ions.

The behaviour of rubidium and potassium with respect to tungsten has been examined by Killian.\* The ionization potentials of rubidium and potassium (4.16 volts and 4.32 volts respectively) are smaller than the work function or electron affinity of tungsten (4.52 volts), so that it may be expected in these cases that at high temperatures, i.e. with a practically clean filament surface, all atoms which strike the filament will be ionized, and will evaporate as ions. Killian found this to be true; the cases are quite analogous to that of caesium. In Fig. 41 some of Killian's results for rubidium on a tungsten filament are reproduced.

Recently Copley and Phipps† published new measurements of the ionization of potassium atoms striking a heated tungsten filament. According to Reimann‡ their results can be explained by assuming a dependence of  $\phi_0$  on temperature (cf. § 7).

When a tungsten filament is heated in rubidium vapour whose pressure is given by the temperature of the walls of the

\* Th. J. Killian, *Phys. Rev.* **27**, 578 (1926).

† M. J. Copley and T. E. Phipps, *Phys. Rev.* **45**, 344 (1934).

‡ A. L. Reimann, *Phys. Rev.* **45**, 898 (1934).

tube (for instance  $39.2^\circ\text{C}$ . for the right-hand curve in Fig. 41), then at relatively low temperatures the filament will be covered to a great extent with rubidium, whereby the work function becomes lower than the ionization potential of the rubidium. This does not mean that absolutely no positive ions will evaporate when the filament is made positive with respect to the surrounding cylinder, but only that the number of positive ions evaporating is small in comparison to the number

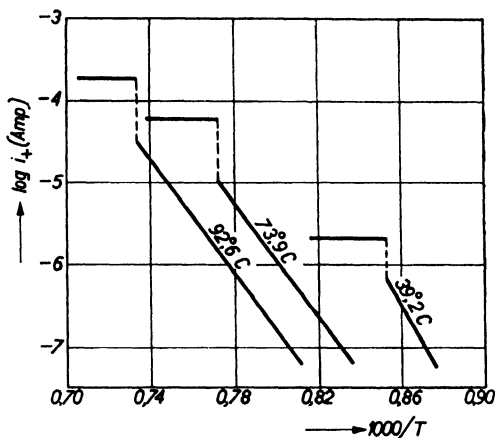


Fig. 41. Current, due to positive rubidium ions, emitted from a tungsten filament in rubidium vapour as a function of filament temperature and vapour pressure of Rb; according to Th. J. Killian.

of neutral atoms evaporating. The ratio of the two rates of evaporation  $\frac{E_{\text{ion}}}{E_{\text{atom}}}$  is given by the Maxwell relation

$$\frac{E_{\text{ion}}}{E_{\text{atom}}} = f e^{\frac{\epsilon(\phi_\theta - V_i)}{kT}},$$

in which  $\phi_\theta$  represents the work function when the fraction of the surface covered is  $\theta$ ,  $V_i$  stands for the ionization potential, and  $f$  is a proportionality factor. As long as  $\phi_\theta < V_i$  this ratio is very much smaller than 1. When the filament temperature is raised,  $\theta$  decreases (see, for example, Fig. 27, § 25) and  $\phi_\theta$  increases proportionally; the relation changes in favour of the ion evaporation. As with caesium, at a definite temperature the point is reached where a slight increase of temperature causes a sudden great increase in the positive-ion current,



since we have reached that region where the evaporation as positive ion exceeds the evaporation as atom ( $\phi_\theta > V_i$ ), and the rate of evaporation of ions increases with decreasing  $\theta$ . The filament is then almost completely freed of rubidium, as we have seen also to be the case with caesium in §§ 25 and 29. If the temperature of the filament is still further increased, all the rubidium atoms striking it will be ionized and the positive-ion current will be controlled by the vapour pressure of the rubidium only, and no longer by the temperature of the filament. This brings us to the horizontal part of the curve (see Fig. 41). At a higher temperature of the tube and thus a higher vapour pressure of rubidium, this process takes place only at higher filament temperatures.

The behaviour of potassium with respect to other metals than tungsten, for instance with respect to molybdenum and tantalum, has been examined by Miss Meyer\*. Her results, including those with tungsten as a supporting metal, are not in complete agreement with the results of Langmuir and of Becker. Thus it was found that when the filament was heated in potassium vapour at various temperatures, the maximum electron emission always appeared at the same temperature independent of the potassium vapour pressure. The maximum emission at a given vapour pressure is reached at that temperature (see also § 38) at which the dynamic equilibrium between the atoms arriving at the filament and those evaporating from it just maintains the  $\theta$  which corresponds to the minimum of the work function. It may therefore be expected that at higher vapour pressures this maximum emission will also occur at higher temperatures of the filament, a fact which has been proved in every case by Langmuir and his co-workers, and by Becker.†

The case of potassium on molybdenum is especially interesting, since the ionization potential of potassium (4.32 volts) is only slightly different from the electron affinity of moly-

\* E. Meyer, *Ann. Phys.*, Lpz. (5), 4, 357 (1930).

† N. D. Morgulis, *Phys. Z. d. Sowj. Union*, 5, 221 (1934), examined the ionization of Na atoms on a tungsten surface. He confirms the results of Langmuir and of Becker.

bdenum (4.41 volts). Miss Meyer found an ion current which does not correspond to the above-mentioned formula, while she also found a different value for the work function. For that reason Evans\* again carefully examined the ionization of potassium on molybdenum filaments. He found that if the vapour-pressure formula of Edmundson and Egerton† holds,

$$\log p \text{ (mm. Hg)} = -\frac{4507}{T} + 7.3447,$$

the ionization in this case is complete. However, in order to attain complete ionization at  $1000^\circ \text{K.}$  the quantity  $\phi_0 - V_i$  must be greater than 0.3 volt according to the formula at the beginning of this section, so that the work function of molybdenum would be more than 4.6 volts. If one uses the vapour-pressure values of Killian,‡

$$\log p \text{ (mm. Hg)} = -\frac{4964}{T} + 8.71,$$

Evans finds that at  $\sim 1000^\circ \text{K.}$  70 per cent. of the potassium atoms are ionized, which leads to the value  $\phi_0 - V_i = 0.1$  volt, and to the value for the work function  $\phi_0$  of molybdenum of 4.42 volts, which agrees very well with the experimentally found value for molybdenum of  $\phi_0 = 4.41$  volts (see § 7).

From the experiments of Moon§ it may be concluded that caesium is strongly ionized at sufficiently high temperatures on a nickel surface ( $\phi_0 = 5.01$  volts), while with potassium the nickel surface must be distinctly hotter before ionization sets in.

When surfaces of platinum, copper or aluminium which are covered with sodium are bombarded with positive ions, adsorbed ions and atoms will be shot away from the surface. If an adsorbed  $\text{Na}^+$  ion is shot away and the work function of the surface is less than the ionization potential of sodium, then there is a great chance that the ion which was knocked off will be neutralized and evaporate further as an atom. As can be

\* R. C. Evans, *Proc. Camb. phil. Soc.* **29**, 522 (1933).

† W. Edmundson and A. Egerton, *Proc. roy. Soc. A*, **113**, 520 (1927).

‡ Th. J. Killian, *Phys. Rev.* **27**, 578 (1926).

§ P. B. Moon, *Proc. Camb. phil. Soc.* **27**, 570 (1931).

seen directly from the potential curves so often referred to, this neutralization can occur only at some distance from the surface, or in other words only at that point where the potential curve for the sodium ion extends above that for the sodium atom (cf. Fig. 24 in § 20). Mayer\* found that in such cases the neutralizing electron does not immediately attain the normal state of the thus-formed atom, but that excited states (see § 11) first occur, and thereafter upon emission of light (for example the sodium D line) the electron reaches the normal state. This emission of light is a very nice indication that  $\text{Na}^+$  ions really do evaporate and are later neutralized. When the filaments used by Mayer were practically free of alkali metal he found no emission of light, since the work function is then higher than the ionization potential and no neutralization takes place. As  $\theta$  increases the phenomenon of light emission begins to appear, increases to a maximum, and then decreases practically to zero. At this last point the work function is still, to be sure, low enough to neutralize ions, but at higher values of  $\theta$  practically only atoms are shot off the surface, since the work of breaking loose has become so much smaller for an atom than for an ion. The fact that in the bombardment by  $\text{K}^+$  ions of a surface upon which  $\text{Na}^+$  ions were adsorbed only sodium light and no potassium light was observed, proves that it really is the adsorbed ions which are shot off and that the case is not one of neutralization of the positive ions striking the surface.

### § 32. The adsorption of barium on tungsten.

The adsorption of barium on tungsten has been examined by Becker.† The ionization potential of barium (5.19 volts) is higher than the electron affinity of tungsten (4.52 volts), so that practically no evaporation of positive barium ions can be expected at high temperatures. This last is, however, the only point in which the adsorption of barium on tungsten differs from that of caesium on tungsten. Becker's experiments show that the electron emission can be increased in the same

\* H. Mayer, *Phil. Mag.* (7), **16**, 594 (1933).

† J. A. Becker, *Trans. Amer. electrochem. Soc.* **55**, 153 (1929).

manner as with caesium on tungsten; here also the specific decrease in work function with increasing proportion of the surface covered is greater at small values of  $\theta$  than at larger values of  $\theta$ . Finally, a maximum in the electron emission is reached here also, and thus a minimum of the work function. Becker considers that in this case also the minimum work function corresponds to a monatomic covering of the surface; this is presumably not so, and the proportion of the surface covered is probably less. Such determinations of  $\theta$  as in the case of caesium are difficult, although a relative surface covering  $\frac{\theta}{\theta_m}$  ( $\theta_m$  is the  $\theta$  corresponding to the minimum work function) can be deduced from Becker's measurements.

Since it is very probable that barium ions do exist on the surface, a supposition that Becker also makes, we shall first attempt to estimate the energies which play a part. We can make a preliminary estimation of the adsorption energy of a barium atom on a tungsten surface, as with caesium on tungsten (§ 27), from the relation

$$Q_a \sim \frac{1}{2} \sqrt{L_{Ba} \times L_W} \cong \frac{1}{2} \sqrt{2.13 \times 9.6} \cong 2.25 \text{ electron volts.}$$

If the barium atom by giving up one electron is adsorbed as a singly charged positive ion  $I - e\phi = 5.19 - 4.52 = 0.67$  electron volt will be necessary, while the adsorption energy  $Q_i$  of the ion will be gained. If this  $Q_i$  is at first calculated only from the mirror image attraction, and the radius of the singly charged positive barium ion is set equal to  $1.6 \text{ \AA.}$ , as is done by Becker, then  $2.25$  electron volts is also obtained for this work. Starting from a free atom and a clean tungsten surface we should thus gain  $2.25$  electron volts upon adsorption as atom, and only  $2.25 - 0.67 = 1.6$  electron volts upon adsorption as ion. From this result we are compelled to conclude that the adsorption does not take place as single charged barium ions.

We have, however, seen in § 11 that in the formation of chemical compounds barium gives up two electrons and forms an ion with the rare gas configuration. For the giving up of these electrons  $5.19 + 9.95 = 15.14$  electron volts must be supplied; the taking up of the two electrons by the tungsten

gives a gain of  $2 \times 4.52 = 9.04$  electron volts, while  $Q_i$  can be calculated in this case to be 10 electron volts. The total energy gained by the adsorption as  $\text{Ba}^{++}$  ions is

$$Q_i + 2\epsilon\phi_0 - I_I - I_{II} = 3.9 \text{ electron volts,}$$

an energy that is 1.65 electron volts greater than that gained by the atom adsorption. We may thus conclude that barium is probably adsorbed in the form of  $\text{Ba}^{++}$  ions at the beginning. In Fig. 42 the potential curves for this case are reproduced.\*

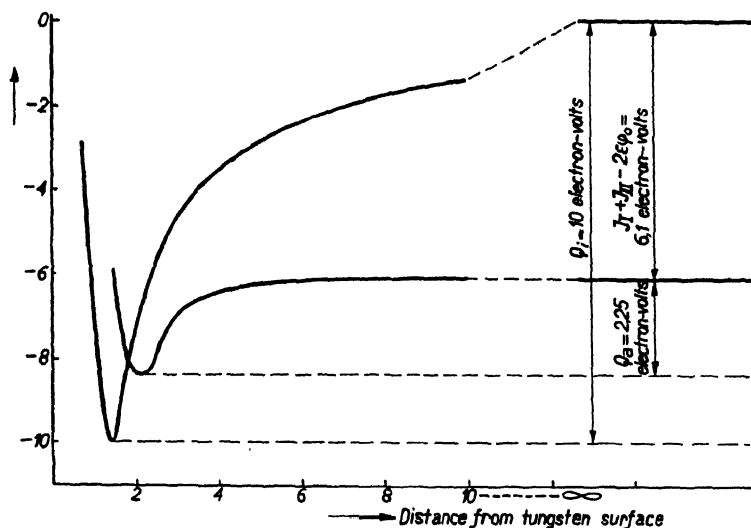


Fig. 42. Potential curves, referring to the adsorption of Ba atoms and  $\text{Ba}^{++}$  ions on a W surface.

Just as in the case of the adsorption of caesium on tungsten, this ion adsorption will continue until the gain in energy by the adsorption as double positive ion is decreased so much by the lowering of the work function, that the gain in energy by the adsorption of an atom next to a positive ion exceeds the former gain. The lowering of the work function will then continue because of the favourable polarization of the barium atoms until here also a minimum is reached, after which, with increasing  $\theta$ , the work function increases.

Becker exposed the tungsten surface for varying lengths of time to a constant supply of barium atoms. If we call the time

\* J. H. de Boer and C. F. Veenemans, *Physica*, 1, 753 (1934).

of exposure which is necessary to reach the maximum emission  $t_m$ , and the fraction of the surface covered at the maximum emission  $\theta_m$  as above, then the relation  $\frac{\theta}{\theta_m}$  can be deduced from the time of exposure  $t$  for a given determination, since this quotient is equal to  $\frac{t}{t_m}$ . From Becker's measurements it ap-

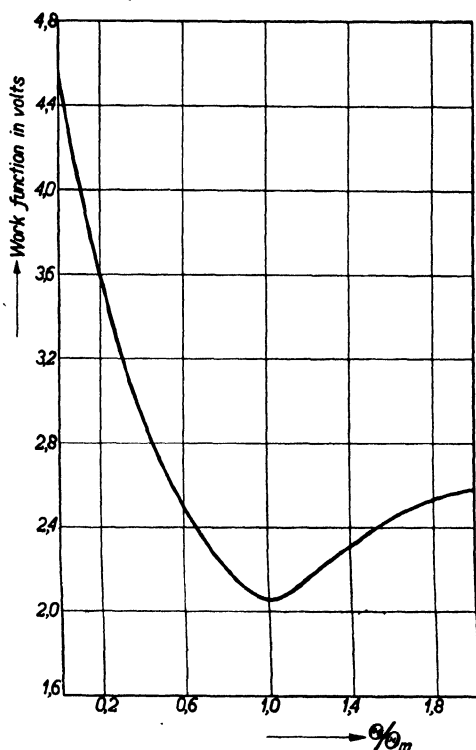


Fig. 43. Work function of a [W]-Ba cathode as a function of  $\theta$ , according to J. A. Becker, *Trans. Faraday Soc.* **28**, 151 (1932).

pears that the lowering of the work function to the point where  $\frac{\theta}{\theta_m} = 0.2$  may be represented by a straight line (see Fig. 43).

As a first approximation we may assume that up to this fraction of the surface covered ions are adsorbed on the surface. Each ion contributes as active dipole the following amount:

$$\mu = 2\epsilon r_{\text{Ba}^{++}} - \frac{2\alpha\epsilon}{(2r_{\text{Ba}^{++}})^2} = 11.6 \times 10^{-18} \text{ e.s.u.}$$

When  $\frac{\theta}{\theta_m} = 0.2$  the lowering of the work function  $\Delta\phi$  equals 0.9 volt. If we call the amount of  $\text{Ba}^{++}$  ions per  $\text{cm.}^2$   $\sigma$ , then at that moment

$$\Delta\phi = 0.9 = 300 \times 4\pi\sigma\mu,$$

from which it follows that  $\sigma = 2.06 \times 10^{13}$  ions/ $\text{cm.}^2$ . The maximum lowering of the work function is reached at  $\frac{\theta}{\theta_m} = 1$ , or at a value of  $\sigma$  like the following:

$$\sigma_{\text{max.}} = 10.3 \times 10^{13} \text{ atoms + ions/cm.}^2,$$

whereby we may again assume that each ion is surrounded by four favourably polarized atoms. If the distribution of the barium on the surface is controlled by the underlying tungsten layer, as was the case with caesium, and the monatomic layer is reached when  $\sigma_{\text{monat.}} = 3.56 \times 10^{14}$  atoms/ $\text{cm.}^2$ , then the maximum lowering of the work function would be reached at  $\theta_m = 0.29$ .

Ryde and Harris\* too have measured the electron emission of [W]-Ba cathodes; they found  $\phi_{\text{min.}}$  to be 1.56 volts.

A cathode, consisting of a base metal  $M$  and ions or atoms  $A$  adsorbed on the surface of  $M$ , will be denoted by the symbol  $[M]-A$  cathode. Thus in Chap. III we were dealing with [W]-Cs cathodes, in this section with [W]-Ba cathodes, and in § 33 we shall treat the [W]-Th cathode and so on.

### § 33. Thorium on tungsten.

Other atoms than those of the alkali or alkaline earth groups can cause by their adsorption on a metal surface such as tungsten or molybdenum a strong lowering in the work functions of those metals. A well-known case is the adsorption of thorium on a tungsten surface. Because of the technical importance of thoriated tungsten filaments this problem, like that of caesium on tungsten, has been investigated in detail. Since these investigations in many respects do not teach us anything new after our treatment of the adsorption of the

\* J. W. Ryde and N. L. Harris, mentioned by E. K. Rideal, *An Introduction to Surface Chemistry*, p. 224, Cambridge (1930); cf. also A. L. Reimann, *Thermionic Emission*, pp. 159-177 (1934).

alkali and alkaline earth metals, we shall discuss them quite briefly and emphasize only those points which are important for our purpose. We are permitted to do this more especially since in 1928 and in 1930 very good surveys of the [W]-Th emitter were written.\*

In most of the experiments the thorium atoms were not adsorbed out of the gas phase as were the alkali metal atoms, nor were they distilled from an external source upon the filament as with barium, but they were allowed to diffuse from within the metal to the surface. In the incandescent lamp industry tungsten filaments are used which contain a small quantity (1 per cent. for example) of thorium oxide to prevent offsetting of the filaments. Langmuir and Rogers† discovered in 1913 that by a suitable temperature treatment of these filaments a very large increase in the electron emission could be obtained. This problem was first studied in detail by Langmuir‡ in 1923, when he laid the foundations for the [W]-Th emitter.

The thorium oxide still exists as  $\text{ThO}_2$  in a tungsten filament which has not been heated to glowing at a high temperature, while  $\text{ThO}_2$  crystallites occur also in tungsten single crystal filaments such as the so-called Pintsch filaments. They have no definite orientation with respect to the surrounding tungsten crystal.§ When the filament is heated above 2500 or 2600° K., part of the thorium oxide is reduced by the tungsten, and thorium atoms are formed.|| From the thorium oxide crystallites there are formed some crystallites of metallic thorium and some products with an oxygen content between Th and  $\text{ThO}_2$ . During this reduction process—at least in the case of polycrystalline filaments—thorium atoms diffuse very quickly out toward the surface. At these high temperatures,

\* W. Schottky and H. Rothe, *Handbuch der Experimentalphysik*, **13**, 2, p. 168 (1928); S. Dushman, *Rev. Mod. Phys.* **2**, 398 (1930).

† I. Langmuir and W. Rogers, *Phys. Rev.* **4**, 544 (1914).

‡ I. Langmuir, *Phys. Rev.* **22**, 357 (1923).

§ Cf., for example, W. G. Burgers and J. A. M. van Liempt, *Z. anorg. Chem.* **193**, 144 (1930).

|| Cf. C. J. Smithells, *J. chem. Soc.* **121**, 2236 (1922); W. Geiss and J. A. M. van Liempt, *Z. anorg. Chem.* **168**, 107 (1927).



however, the thorium atoms do not remain adsorbed on the surface, but quickly evaporate. At the end of the reduction process the surface of the tungsten filament is thus still practically clean. If the temperature of the filament is now reduced to  $2100^{\circ}\text{K.}$  for instance, a relatively rapid diffusion of the thorium atoms toward the surface still continues, while now the rate of evaporation is so much lower that the atoms arriving at the surface from within remain adsorbed. A dipole layer is thus formed which increases the electron emission, so that the filament can be said to be activated by this treatment. By sufficiently long treatment in this temperature region the fraction of the surface covered becomes such that the most favourable lowering of the work function is about attained. At a still lower temperature ( $1500^{\circ}\text{K.}$ ) the state of the filament no longer changes, so that at this temperature the electron emission can be investigated without a change in the state of the adsorbed layer during the measurements. If it is desired to clean a filament covered with thorium, this can be done by heating it in the temperature range between  $2300$  and  $2600^{\circ}\text{K.}$ ; in this region the rate of evaporation is greater than the rate of diffusion, so that at the surface  $\theta$  is practically zero. Thanks to the differing rates of reduction, evaporation and diffusion, and their differing dependence on temperature, various temperature ranges may be distinguished. The following are due to Dushman:\*

$T \geq 2600^{\circ}\text{K.}$  reduction range,

$T = 2300\text{--}2600^{\circ}\text{K.}$  deactivating range,

$T = 2000\text{--}2300^{\circ}\text{K.}$  activating range,

$T = 1800\text{--}2000^{\circ}\text{K.}$  operating range.

### § 34. The diffusion of thorium through the tungsten filament.

In his detailed study of the process of activation at various temperatures Langmuir† used the electron emission as a measure of the fraction of the surface covered. This means that it was assumed that the lowering of the work function  $\Delta\phi_{\theta}$  increased linearly with  $\theta$  over the whole range from  $\theta = 0$  to

\* S. Dushman, *Rev. Mod. Phys.* **2**, 399 (1930).

† I. Langmuir, *Phys. Rev.* **22**, 357 (1923).

$\theta = 1$ , so that the logarithm of the electron emission would also increase proportionally to  $\theta$ . If the electron emission when  $\theta = 0$ , i.e. for clean tungsten, is known ( $i_0$ ), and also that when  $\theta = 1$ , for the completely covered filament ( $i_1$ ), then from the measured value  $i_\theta$  one may calculate the corresponding value of  $\theta$  by means of the relation

$$\theta = \frac{\log i_\theta - \log i_0}{\log i_1 - \log i_0}.$$

Langmuir found that  $\theta$  defined in this manner did not increase linearly with the time if the diffusion was allowed to complete itself at a constant temperature, but that the course of the activating curve can be represented by the empirical relation

$$\theta = 1 - e^{-ct},$$

where  $t$  is the time and  $c$  a constant. From this relation follows

$$\ln(1 - \theta) = -ct,$$

or by differentiating

$$\frac{d\theta}{dt} = c(1 - \theta).$$

According to this last equation the increase in the fraction of the surface covered per unit of time should be proportional to the part of the surface still clean ( $1 - \theta$ ). In order to explain this Langmuir assumed that the atoms coming out of the filament remain fixed on the surface at the spot where they first reach the surface from the inside, and that there is no migration, while, further, an atom which comes out on the surface just under another atom already adsorbed will cause the latter to evaporate and will take its place on the surface. This principle of induced evaporation depends very much upon a homogeneous diffusion through the filament and upon the absence of migration on the surface.

The problem of diffusion has been investigated by Clausing\* upon the instigation of G. Holst. When a polycrystalline tungsten filament containing  $\text{ThO}_2$  is provided with a  $\text{ThO}_2$ -free polycrystalline tungsten coating, after reduction of the thorium oxide and activation, a high emission, normal for

\* P. Clausing, *Physica*, 7, 193 (1927).

thoriated tungsten filaments, can be obtained. The thorium thus diffuses normally through the tungsten coating to the outside. When, however, a Pintsch single crystal filament containing  $\text{ThO}_2$  is covered with pure tungsten by the thermal dissociation of  $\text{WCl}_6$ , then the coating itself also becomes monocrystalline.\* Although Pintsch filaments themselves may be easily activated, Clausing found that it was impossible to activate the coated Pintsch filaments; the thorium did not diffuse through the monocrystalline tungsten covering. If the covering was removed by cathode sputtering in an argon discharge, the Pintsch filament could then be activated normally. From these experiments the important conclusion may be drawn that the thorium atoms do not choose their paths toward the surface through the tungsten lattice, but along the crystal boundaries of the polycrystalline material. We are thus concerned not with a pure diffusion but with a surface migration along the intercrystalline surfaces. When the thorium has reached the surface it must here also spread itself out by surface migration to form a homogeneous covering.

Gehrts† attempted to reconcile the two principles brought forward by Clausing (diffusion along crystal boundaries and surface mobility) with Langmuir's activation curves, without having recourse to the principle of induced evaporation. More recent research has shown, however, that the original assumption of Langmuir, that  $\Delta\phi_0$  increases proportionally with  $\theta$ , is incorrect,‡ so that the determination of  $\theta$  which depends on this assumption does not give valid results. Brattain and Becker§ have examined in detail the connection between the fraction of the surface covered and the electron emission (see also § 35), and were able to study the activation curves anew in the light of their investigations. It appeared that  $\theta$  increased quite linearly with the time until the evaporation from the surface at higher values of  $\theta$  began to be appreciable. This meant that the induced evaporation which Langmuir conceived on the

\* A. E. van Arkel, *Physica*, **3**, 76 (1923).

† A. Gehrts, *Z. tech. Phys.* **12**, 66 (1931).

‡ Cf. J. A. Becker, *Trans. Faraday Soc.* **28**, 148 (1932).

§ W. H. Brattain and J. A. Becker, *Phys. Rev.* **43**, 428 (1933).

basis of the original activation curves does not in reality exist, but that the form of the curves must be ascribed to the non-linearity of the relation between  $\Delta\phi_\theta$  and  $\theta$ , as was also the case with caesium and barium.

One still frequently meets in the literature the view that although the thorium diffuses very quickly along the crystal boundaries, it does also diffuse slowly through the tungsten lattice.\* An argument against this view is the fact that the temperature coefficient of the electrical resistance of tungsten which contains  $\text{ThO}_2$  and of tungsten in which a considerable amount of metallic thorium is produced by the reduction of  $\text{ThO}_2$  are completely unchanged with respect to pure tungsten.† This quantity is a sensitive measure of the formation of mixed crystals, which must be assumed to be present to a certain extent if there is a diffusion of thorium through the crystal lattice itself. The lack of change in the temperature coefficient of the electrical resistance thus indicates the absence of mixed crystals, and consequently the absence of diffusion *through* the lattice.

Fonda, Young and Walker‡ concluded from their measurements that the product of the diffusion constant and the square of the grain radius, with thoriated tungsten filaments of various grain sizes, was constant, and that therefore the diffusion must take place within the grain. If this observation is confirmed over a long range of grain sizes, the conclusion would rather be that the diffusion takes place between the crystals, not along the intercrystalline surfaces, but along the edges of the crystallites, since the total combined length of the edges decreases as a square with increasing grain radius. A movement along the ribs instead of along the surfaces would be in good agreement with the observations of § 14.

\* Cf., for instance, I. Langmuir, *Angew. Chem. Nobel Lecture*, **46**, 721 (1933); *Chem. Rev.* **13**, 147 (1933).

† W. Geiss and J. A. M. van Liempt, *Z. anorg. Chem.* **168**, 111 (1927).

‡ G. R. Fonda, A. H. Young and Amy Walker, *Physics*, **4**, 3 (1933).

### § 35. The evaporation of thorium from tungsten; electron emission as a function of $\theta$ .

In § 33 it was stated that the activating range is distinguished by the absence of a noticeable evaporation of the thorium atoms which diffuse out to the surface from within the filament. The thorium atoms which reach the surface in excess of those needed to form a monatomic layer do indeed evaporate, while at the higher temperatures of the deactivating range the thorium atoms which form the monatomic layer also evaporate. From the dependence on temperature of this rate of evaporation Langmuir\* deduced a heat of evaporation of 204 kg. cal./gr. atom = 8.85 electron volts/gr. atom. This is a high value when we consider that the heat of evaporation of pure tungsten is 221 kg. cal./gr. atom = 9.6 electron volts/gr. atom, and of pure thorium† 145 kg. cal./gr. atom = 6.3 electron volts/gr. atom. If the thorium were adsorbed only by van der Waals' attractive forces as atom, we should expect a value of the heat of adsorption

$$Q_a \sim \frac{1}{2} \sqrt{L_{\text{Th}} \times L_{\text{W}}} \\ = \sim \frac{1}{2} \sqrt{6.3 \times 9.6} = \sim 3.9 \text{ electron volts/gr. atom.}$$

Just as with caesium and barium on tungsten a much higher (more than double) value is actually found. On the basis of this we may here also suspect that the thorium atoms are adsorbed not as atoms but as ions, and by analogy with barium we might suspect that they are adsorbed as multiple charged positive ions.

Brattain and Becker‡ studied the adsorption of thorium on tungsten in a manner similar to that used for the study of barium on tungsten. They evaporated thorium from a glowing thorium wire upon a tungsten ribbon, and measured the electron emission of the tungsten surface after various known lengths of time  $t$  during which the thorium wire had been heated to glowing. After a definite time  $t_m$  the electron emis-

\* I. Langmuir, *Phys. Rev.* **22**, 391 (1923).

† C. Zwicker, unpublished; for the slope of the line of vapour pressure see *Physica*, **8**, 241 (1928).

‡ W. H. Brattain and J. A. Becker, *Phys. Rev.* **43**, 428 (1933).

sion of the thus thoriated tungsten surface passed a maximum. The fraction of the surface covered,  $\theta_m$ , which corresponds to the time,  $t_m$ , may be thus considered to cause the greatest lowering of the work function. Brattain and Becker again identify this  $\theta_m$  with the complete monatomic covering of the surface; experience has shown us in the cases of caesium and barium that there is no reason for this. One point is in any case correct, as Brattain and Becker expressly demonstrate, that

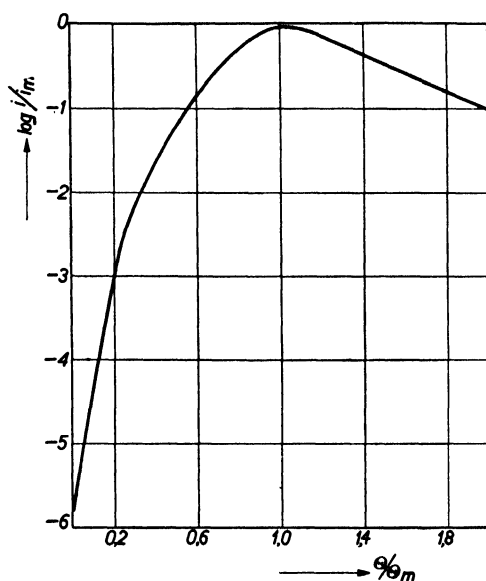


Fig. 44. Variation of electron emission from a thorium-covered tungsten filament as a function of  $\theta$ , according to W. H. Brattain and J. A. Becker, *l.c.*

the value  $\frac{t}{t_m}$  gives very well the value  $\frac{\theta}{\theta_m}$ . By plotting their measured points for the electron emission expressed as  $\log \frac{i}{i_m}$ , where  $i_m$  is the maximum emission, as a function of the values of  $\frac{\theta}{\theta_m}$  the curve reproduced in Fig. 44 may be drawn. The form of this curve is the same as that of caesium on tungsten or of barium on tungsten, so that the analogy with these cases is very striking (see also Fig. 30, § 26).

The study of the rate of evaporation of the thorium in the form of atoms showed once more, as with caesium, that the heat of evaporation as atoms decreases with increasing  $\theta$ .

### § 36. Surface migration.

We have already pointed out several times (§§ 30 and 34) that adsorbed atoms and ions are able to move along the surface on which they are adsorbed. In the case of the adsorption of caesium from the vapour phase, as well as that of the diffusion of thorium from within a tungsten filament to the surface, this surface migration attempts to bring about a homogeneous distribution of the adsorbed atoms. It may be considered that at ordinary temperatures this surface migration is either slight or entirely absent. To be sure the somewhat classic experiment of Volmer and Estermann\* on the condensation of mercury atoms on solid mercury shows that at the low temperatures used the mercury atoms can still migrate a distance of several tenths of a millimetre along the surface, and one might suppose some mobility of caesium on tungsten. A migration of barium or thorium on tungsten at room temperature is less to be expected. At higher temperatures this migration does exist, and its existence has been proved conclusively by the experiments of Becker.† A tungsten ribbon is covered on one side with barium so that the relative degree of covering is  $\frac{\theta}{\theta_m} = 0.8$  (see § 32). The electron emission from both surfaces of the tungsten ribbon is then measured. A value  $i_1$  is found for the side covered with barium which value corresponds to that for  $\frac{\theta}{\theta_m} = 0.8$ , while a value  $i_2$  is found for the other side, which is the emission for pure tungsten. The ribbon is now heated for definite lengths of time to a high temperature, and the emission from each side is measured again. If migration has taken place one observes that the emission from the original barium-covered side decreases, and that from the other side increases, until finally the same value of the emission

\* M. Volmer and I. Estermann, *Z. Phys.* **7**, 13 (1921).

† Compare J. A. Becker, *Trans. Faraday Soc.* **28**, 155 (1932).

is found for both sides, which corresponds to  $\frac{\theta}{\theta_m} = 0.4$  (see Fig. 45).

In the case of barium on tungsten it was found that at  $900^\circ\text{K}$ . the migration proceeded at an appreciable velocity, while only above  $1150^\circ\text{K}$ . does evaporation become important.\* In the case of thorium on tungsten the migration occurred at an appreciable rate above  $1655^\circ\text{K}$ . In order that the thorium atoms (ions) may move along the surface, an opposing energy of about 4.8 electron volts for every jump must be

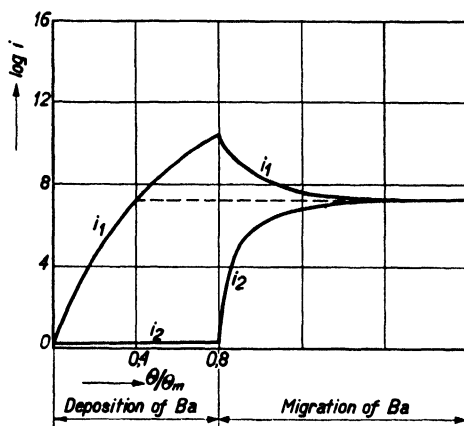


Fig. 45. Deposition and migration of barium on tungsten.  
Becker, *Trans. Faraday Soc.* **28**, 155 (1932).

overcome,† a quantity which agrees completely in order of magnitude with Langmuir's "heat of diffusion", which was 4.1 electron volts. We have seen that this "diffusion" must also be considered as a case of migration along the surfaces (or edges) of the crystallites (§ 34).

In § 30 it was stated that in the migration of caesium ions on tungsten an energy of 0.61 electron volt must be overcome.

In the cases of the adsorption of oxygen on tungsten and of platinum‡ on tungsten which we shall discuss later (§§ 46 and

\* J. A. Becker, *Trans. Amer. electrochem. Soc.* **55**, 153 (1929).

† W. H. Brattain and J. A. Becker, *Phys. Rev.* **43**, 445 (1933).

‡ R. W. Sears and J. A. Becker, *Phys. Rev.* **43**, 1058 (1933).



52) Becker showed in the above-mentioned way that migration of the adsorbed particles takes place.

**§ 37. The electron emission of surfaces covered with a monatomic layer of electropositive ions in an accelerating field.**

The subject of the electron emission of these adsorbed layers in accelerating fields must be briefly touched upon. We have seen in § 9 that due to the Schottky effect the thermionic or photoelectric current is not saturated but continues to increase with increasing field in such a way that the logarithm of the emission current increases with the square root of the field strength.

With surfaces whose work function is very much lowered by adsorption of electropositive atoms, the saturation appears to be even less perfect, so that the current increases more strongly with the field than Schottky's relation would indicate. These discrepancies with the normal increase of the emission current as given by the Schottky relation are especially great when the fraction of the surface covered is smaller than that which causes the maximum lowering of the work function; when  $\frac{\theta}{\theta_m}$  approaches zero or one, the discrepancies are smaller.

As early as 1920 Langmuir\* attempted to explain this phenomenon by assuming that the electropositive atoms are gathered together in groups or patches which are electropositive with respect to the base material between the patches. Thus there are adjacent portions on the surface which exhibit a difference of potential due to their difference in work function (§ 10). By means of these potential differences electric fields are created above the surface which oppose the electron emission of the electropositive patches, while they favour the emission of the electronegative non-covered areas. These fields are in general observable at distances from the surface which are comparable with the dimensions of the patches themselves, just as the field of an ionic double layer (see § 18) is still ap-

\* I. Langmuir, *Gen. elect. Rev.* **23**, 504 (1920).

preciable at a distance comparable with the separation of the ions in the layer.

Becker and Mueller\* determined the field which causes these discrepancies with the Schottky effect, and they found that even at a distance of  $10^{-4}$  cm. a field of about 1000 volts/cm. was present, while at that distance the field due to the mirror image attraction was only about  $3\frac{1}{2}$  volts/cm.

On the basis of certain assumptions about the size of the patches and the potential difference between the different parts of the surface, Langmuir† comes to the conclusion that the discrepancies with the Schottky effect must be small with small electric fields and increase with the field strength. The measurements of Reynolds‡ on tungsten partially covered with thorium had, however, shown that the discrepancies were the greatest with small fields, while for field strengths exceeding about 10,000 volts/cm.,  $\log i$  increases proportionally with  $\sqrt{F}$ , and thus satisfies the Schottky equation. Compton and Langmuir then decided that the theory of patches does not succeed in explaining the discrepancies with the Schottky effect.

On the other hand, Linford§ and at the same time Becker and Rojansky|| came to the conclusion that the experimentally found curves could well be explained if one assumes that the size of the patches is such that they have a radius equal to about  $10^{-4}$  cm. and that the potential differences on the surface are relatively small (several tenths of a volt). If the patches have a radius of  $1.8 \times 10^{-4}$  cm. and there is a difference of potential between the different kinds of patches of 0.36 volt, then the observed and the calculated curves are almost exactly alike. Since the total lowering of the work function in the adsorption of thorium on tungsten is about 1.5 volts, this means that the distribution of the thorium atoms on the

\* J. A. Becker and D. W. Mueller, *Phys. Rev.* **31**, 341 (1928).

† Cf. K. T. Compton and I. Langmuir, *Rev. Mod. Phys.* **2**, 150-160 (1930), in which a good survey up to 1930 is given.

‡ N. B. Reynolds, *Phys. Rev.* **35**, 158 (1930).

§ L. B. Linford, *Phys. Rev.* **37**, 1018 (1931).

|| J. A. Becker and V. Rojansky, mentioned in a survey by L. B. Linford, *Rev. Mod. Phys.* **5**, 50 (1933).

surface is not such that all the thorium atoms are present within the patches, and none in the spaces between, but rather that the thorium atoms are distributed over the whole surface, and that there are only differences in the density of covering. According to Becker there is a correlation between the crystal size of the tungsten crystals on the surface of the filament and the size of the patches. It is very possible that the ribs of the tungsten crystals on the surface are more thickly covered than the rest with adsorbed ions and atoms (cf. §§ 14 and 34).

In accordance with this Brüche and Johansson\* state that the emission of a [Ni]-Ba cathode is not homogeneously distributed over the whole surface of the cathode, and that the image of this distribution is the same as the pattern obtained by etching of the nickel base metal.

**§ 38. Some data on the electron emission of metallic surfaces covered with ions of electropositive metals.**

Since the logarithm of the electron emission increases linearly with the work function, it is evident that due to these electropositive double layers the electron emission at one and the same temperature must increase enormously. The electron emission of a tungsten filament increases, for example, at 650° K. by a factor  $10^{20}$ , when the filament is surrounded by caesium vapour at room temperature, which gives exactly that covering of the surface which causes the maximum lowering of the work function. At 1500° K. the electron emission of a thorium-covered tungsten filament is  $10^5$  times that of an ordinary tungsten filament.

When a tungsten filament is heated in caesium vapour at the first low temperature the filament will be covered with a considerable amount of adsorbed caesium. With rising temperature the electron emission will increase, not only due to the higher temperature, but also because the fraction of the surface covered decreases so that ( $\theta$  in the beginning was greater than  $\theta_m$ ) the work function decreases. By a continual raising of the temperature,  $\theta_m$  can be finally reached, and thereafter upon further rise in temperature  $\theta$  will become smaller

\* E. Brüche and H. Johansson, *Z. Phys.* **84**, 56 (1933).

than  $\theta_m$ , which will cause the work function to increase again. The result of this is that the electron emission increases less rapidly at first, then passes through a maximum, and finally with continually increasing temperature decreases. In the end at high temperatures an entirely clean tungsten filament is obtained, and we reach the emission curve of pure tungsten (see line *a* in Fig. 46). At a higher vapour pressure of caesium (at 80° C. for example, see Fig. 46, line *b*) more caesium atoms strike the filament per unit time, and the maximum is therefore

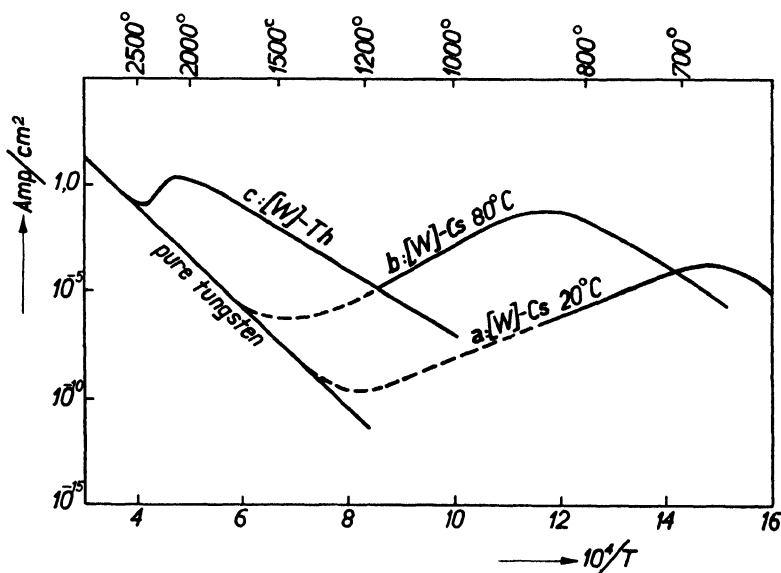


Fig. 46. Electron emission from tungsten filaments, covered with Cs or Th as a function of temperature. I. Langmuir, *Industr. Engng Chem.* **22**, 390 (1930).

only reached at higher temperatures, since the rate of evaporation off the filament is governed only by the filament temperature.

The electron emission from a thorium-covered tungsten filament exhibits in principle the same behaviour. To be sure we are not concerned here with a dynamic equilibrium between adsorbed layer and vapour, but the emission will nevertheless only increase upon increase of temperature, since after the temperature increases the emission reaches a maximum because of the finally resulting importance of the evaporation of the thorium (deactivating range), and then decreases again

in order finally to pass over to the emission of a clean tungsten filament. Thus here again we see an analogy between caesium on tungsten and thorium on tungsten.

The same analogy is striking when, with Becker,\* we plot the work function as a function of the fraction of the surface covered. In order to compare the curves with each other the work function is plotted against  $\frac{\theta}{\theta_m}$  (Fig. 47).

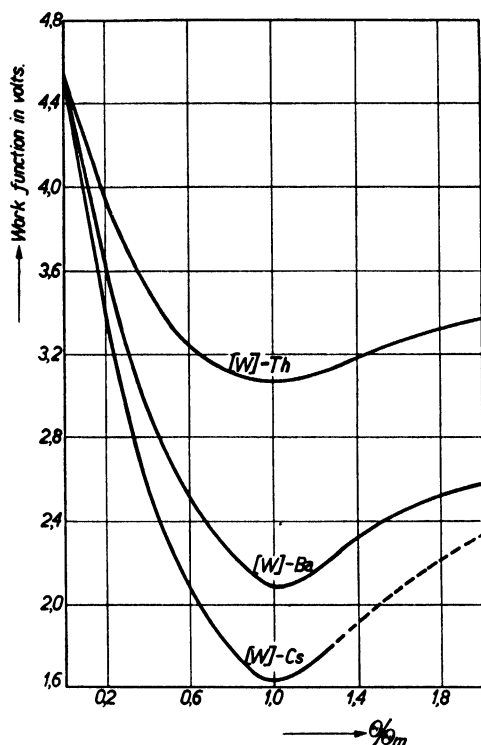


Fig. 47. Work functions of Th, Cs and Ba covered tungsten filaments.\*

In the construction of Fig. 47 it is assumed that the  $A$  value in the emission formula

$$i = AT^2 e^{\frac{-\epsilon\phi}{kT}}$$

is not changed by the fact that the surface is covered with a double layer. This is, as a matter of fact, not true, as  $A$  de-

\* J. A. Becker, *Trans. Faraday Soc.* **28**, 151 (1932).

creases in all these cases with increasing  $\theta$ . Langmuir\* gives for caesium on tungsten in one of his later articles the following values when that fraction of the surface is covered at which the work function reaches its minimum value:

$A_{\min.} = 3.26 \text{ amp. cm.}^{-2} \text{ deg.}^{-2}$  and  $\phi_{\min.} = 1.36 \text{ volts}$ , while as we have seen in § 4  $A$  has a value of  $\sim 120 \text{ amp. cm.}^{-2} \text{ deg.}^{-2}$  for pure metals. The value of  $A$  also decreases to an important degree in the adsorption of thorium on tungsten. Thus Dushman and Ewald† find, for the state in which the work function is lowered the most,

$A_{\min.} = 3.0 \text{ amp. cm.}^{-2} \text{ deg.}^{-2}$  and  $\phi_{\min.} = 2.63 \text{ volts}$ , while Kingdon‡ had already arrived at the following values:

$A_{\min.} = 7 \text{ amp. cm.}^{-2} \text{ deg.}^{-2}$  and  $\phi_{\min.} = 2.69 \text{ volts}$ .

In their detailed investigation in which they evaporated thorium on the tungsten ribbon from the outside Brattain and Becker§ find that the value of  $A$  decreases from  $A = 69$  at  $\theta = 0$  to  $A = 15.5$  at  $\frac{\theta}{\theta_m} = 1$ , while the value again increases to  $A = 65$  when  $\frac{\theta}{\theta_m} = 2$ . At the same time the value of the work function changes from  $\phi = 4.52 \text{ volts}$  for pure tungsten, passing through the value  $\phi = 2.85 \text{ volts}$  when  $\frac{\theta}{\theta_m} = 1$  to  $\phi = 3.27 \text{ volts}$  when  $\frac{\theta}{\theta_m} = 2$ .

The same behaviour is found in the adsorption of metals such as Ce, La,|| etc., as appears from the following table (Table VI) in which for a given emitter the values of  $A$  and  $\phi$  are given when that fraction of the surface is covered at which  $\phi$  is a minimum. It is difficult to decide to what the lowering of the value of  $A$  may be ascribed. We shall return to this question later (§ 49).

\* I. Langmuir, *J. Amer. chem. Soc.* **54**, 2818 (1932).

† S. Dushman and J. W. Ewald, *Phys. Rev.* **29**, 857 (1927).

‡ K. H. Kingdon, *Phys. Rev.* **24**, 510 (1924).

§ W. H. Brattain and J. A. Becker, *Phys. Rev.* **43**, 437 (1933).

|| S. Dushman, D. Dennison and N. B. Reynolds, *Phys. Rev.* **29**, 903 (1927).

Table VI\*

Emitter	$A$ in amp. cm. <sup>-2</sup> deg. <sup>-2</sup>	$\phi$ in volts
[W]-Ce	8.0	2.71
[W]-La	8.0	2.71
[W]-U	3.2	2.84
[W]-Yt	7.0	2.70
[W]-Zr	5.0	3.14
[W]-Th	3.0	2.63
[Mo]-Th	1.5	2.58

Finally, we observe that the emission of a tungsten filament covered with thorium is much higher than the emission of compact thorium itself, which fact appears from the values of the work function. While the work function for the [W]-Th emitter is about 2.7 volts, for pure thorium according to Zwikker†  $\phi = 3.36$  volts. Similar behaviour is found in the cases of all the metals mentioned in this chapter.

\* Table taken from S. Dushman, *Rev. Mod. Phys.* **2**, 403 (1930).

† C. Zwikker, *Proc. Roy. Acad. Amst.* **29**, 792 (1926).

## CHAPTER V

# PHOTOELECTRIC EMISSION AFTER ADSORPTION OF ELECTROPOSITIVE METALS ON METAL SURFACES

### § 39. Introduction.

In the foregoing chapters we were able to construct a satisfactory picture of the adsorption on metallic surfaces from the phenomena of thermionic emission. We must now see to what extent this picture agrees with the results obtained from the study of the photoelectric emission, always keeping in mind that the photoelectrically active surfaces are examined at room temperature, or even in many cases at a much lower temperature, while for the measurements of thermionic emission the surface was always heated to a high temperature. This point is of especial importance for the phenomenon of surface migration which was treated in §§ 30 and 36.

The photoelectric behaviour is dependent upon more different variables than is the thermionic emission. It may be studied as a function of the fraction of the surface  $\theta$  covered with adsorbed material in the same way as the thermionic emission, but at the same time its dependence on the wave-length is very important, as well as its dependence on the temperature of the cathode, and on the direction of the electrical vector of the incident light when polarized light is used, and on the angle of incidence of this light.

We shall see that especially in the cases of the adsorption of the alkali and alkaline earth metal atoms on metal surfaces there are two sources of photoelectrons. In the first place they may be the conduction electrons of the supporting metal as was the case with thermionic emission, or in the second place they may be valence electrons of the adsorbed atoms. The latter is only possible of course when the fraction of the surface  $\theta$  covered with adsorbed material is so large that some atoms are already adsorbed next to the ions which were first adsorbed.



When a portion, or even in some cases all, of the photoelectrons have their source in the valence electrons of the adsorbed atoms this fact will usually be indicated by a so-called "selective photoeffect". In this effect the photoelectric emission does not increase regularly from the photoelectric threshold with decreasing wave-length of light, but the emission increases rapidly at first with decreasing wave-length, then decreases, and very often a minimum of the emission is reached whereafter an increase again follows. If the cathode is optically plane and allows of an experiment with polarized light, it is usually found that when the incident light is polarized in such a way that the electric vector has a component perpendicular to the surface of the cathode, the photoemission is many times greater than for polarized light whose electric vector is parallel to the surface of the cathode. The causes of these selective photoelectric phenomena, which are in general due to an absorption of light by the adsorbed atoms, will not be discussed in this chapter but in Chap. ix, after we have discussed in more detail the light absorption phenomena of adsorbed atoms and molecules in Chap. viii. In this chapter we shall, however, often make use of the fact that the presence of a selective photoelectric effect indicates that there are not only ions but also atoms adsorbed on the surface.

In the following sections we shall take up the change in the photoemission of the supporting metal caused by the adsorption of electropositive atoms.

#### § 40. The changes in the photoelectric emission on the adsorption of electropositive atoms.

Invisibly thin films of, for example, potassium on a metal make this metal photoelectrically sensitive for visible light, as was discovered by Geitel\* in 1922. The anode of a potassium photoelectric cell appeared also to have become photoelectrically sensitive. Upon heating the anode its sensitivity disappeared, and on cooling the sensitivity reappeared again after a few minutes. The thin adsorbed potassium film which forms spontaneously on the anode was the cause of this phenomenon.

\* H. Geitel, *Ann. Phys.*, Lpz., 67, 420 (1922).

In 1924 Ives\* published a very detailed account of his examination of the photoelectric behaviour of such spontaneously formed adsorbed alkali metal films on a large number of supporting metals. When a polished platinum surface is exposed to sodium vapour an adsorbed film of sodium will accumulate slowly. During the formation of this film the surface, which previously possessed no photoelectric sensitiveness for visible light, becomes photoelectrically sensitive. The sensitivity rises to a maximum as the film accumulates and then decreases to a final value which is considerably less than the maximum previously attained. Ives measured the sensitivity in polarized light, which was polarized with the electric vector parallel to

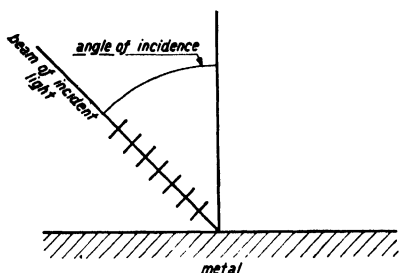


Fig. 48a. Electric vector of the incident light parallel to the plane of incidence.  $\parallel$ .

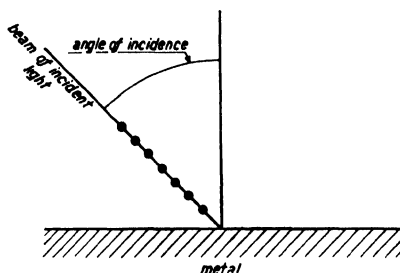


Fig. 48b. Electric vector of the incident light perpendicular to the plane of incidence.  $\perp$ .

the plane of incidence (Fig. 48a), and which will be designated by the symbol  $\parallel$ ; and for light polarized with the electric vector perpendicular to the plane of incidence (Fig. 48b), designated from now on by  $\perp$ . In Fig. 48a the electric vector lies in the plane of the drawing as is indicated, and the electric vector thus has a component perpendicular to the surface of the metal, which component becomes greater as the angle of incidence (angle with the normal to the surface) increases. In Fig. 48b, with  $\perp$  light, the electric vector is perpendicular to the plane of the drawing and is always parallel to the surface. When the angle of incidence is zero,  $\parallel$  light is naturally equivalent to  $\perp$  light. Ives now found that the sensitivity for  $\parallel$  light increased much more rapidly than that for  $\perp$  light when the

\* H. E. Ives, *Astrophys. J.* **60**, 209 (1924).

fraction of the surface covered with sodium increased (Fig. 49).

It must be noted at this point that for  $\perp$  as well as  $\parallel$  light the photoelectric current does not increase linearly with the time, but in the beginning it increases approximately according to an  $e$  power. This was to be expected since we have seen in the foregoing chapters that at the beginning of the adsorption, when only ions are being added to the surface, the work function decreases linearly with increasing  $\theta$  (§§ 18 and 27). Since in the experiment under consideration an equal quantity

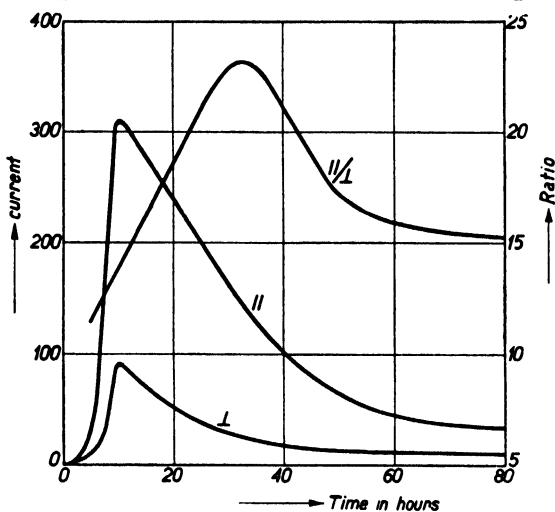


Fig. 49. The progress of photoelectric effect with time; sodium on platinum, according to H. E. Ives, *Astrophys. J.* **60**, 218 (1924).  $\parallel$  at  $80^\circ$  incidence;  $\perp$  at  $0^\circ$  incidence;  $\parallel/\perp$  both at  $80^\circ$  incidence.

of sodium was adsorbed for each unit of time and as the logarithm of the photocurrent changes linearly with  $\Delta\phi$ , and thus at the beginning of the adsorption also linearly with  $\theta$  and with the time, the form of the curve here found was to be expected. If the photoelectrons were supplied already at this stage of the adsorption by the adsorbed atoms, one should have found a linear relation between the photocurrent itself and the fraction of the surface covered, or between the current and the time, since then the photocurrent would have had to be directly proportional to the number of atoms which are effective for the emission of photoelectrons.

In many other cases of adsorption of alkali metal atoms on metal surfaces there is also at the beginning of the adsorption a logarithmic relation between the photocurrent and the fraction of the surface covered. As a further example Fig. 50 shows the change of the photoemission in unpolarized white light with increasing adsorption of sodium on tungsten, as a function of the fraction of the surface covered.\* In all these cases the indications are that we are concerned with an

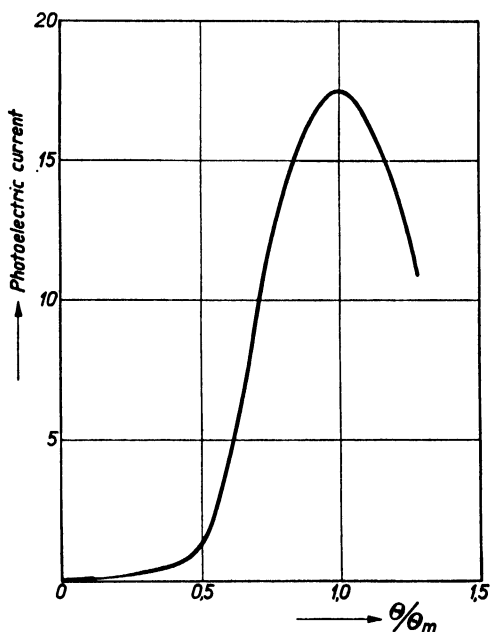


Fig. 50. Variation of photoelectric current with  $\theta$ ; sodium on a tungsten surface.

emission of electrons from the supporting metal. In Fig. 49 it is striking that the ratio  $\parallel/\perp$  increases with increasing surface concentration, and continues to increase even after the maximum emission is reached, until it later reaches a maximum of its own, after which the ratio again decreases. In Fig. 49 the ratio  $\parallel/\perp$  is given for an angle of incidence of  $80^\circ$ . Upon comparison with Fig. 51, in which the dependence of the photo-

\* J. H. de Boer and C. F. Veenemans, will appear shortly in *Physica* 2 (1935).

current on the angle of incidence is given for several stages out of Fig. 49, it may be noted that the ratio at that angle is large because the sensitivity for  $\parallel$  light is so great at an angle of incidence of  $80^\circ$ . That means, therefore, that especially when the component of the electric vector which is perpendicular to the surface is large, the sensitivity is very much increased. As we shall see in §§ 64 and 71, this behaviour may be ascribed to the specific absorption of the thus polarized light by the

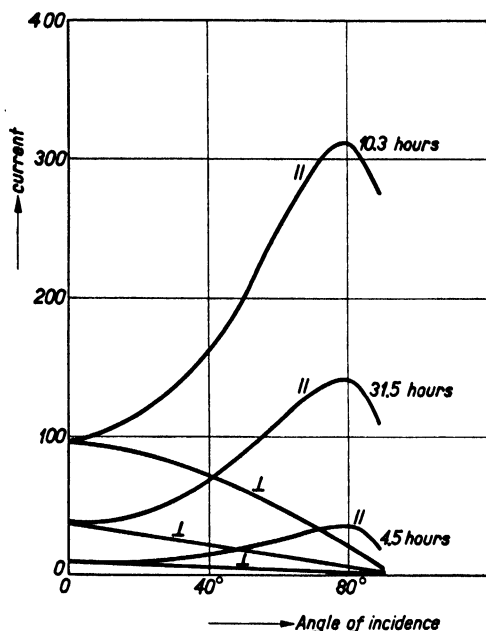


Fig. 51. Variation of photoelectric current with angle of incidence; sodium on platinum. H. E. Ives, *Astrophys. J.* **60**, 218 (1924).

adsorbed atoms. The total course of the curve for  $\parallel$  light points to the selective photoelectric effect, and indicates that at this stage of the adsorption a large portion of the electrons have their source in the adsorbed atoms. This selective photoelectric effect is already present when the maximum of the photoemission is reached, since the large ratio  $\parallel/\perp$  found at that point can no longer be explained from the optical behaviour of the underlying layer.

The other alkali metals on platinum exhibit a similar behaviour. Fig. 52 gives the change in photoelectric sensitivity

by the adsorption of rubidium on platinum. In this case Ives used monochromatic light; from his measurements we have reproduced those for the wave-lengths  $\lambda = 620 \text{ m}\mu$ ,  $\lambda = 440 \text{ m}\mu$  and  $\lambda = 380 \text{ m}\mu$ . The measurements taken with  $\perp$  light exhibit practically the same result as that for sodium on platinum which we have already seen, and represent the normal emission in which electrons come mainly from the platinum metal. The measurements in  $\parallel$  light exhibit this peculiarity, that after the first maximum in the measurements with light of short wave-length, a second maximum follows. The first maximum occurs at the same value of  $\theta$  at which the maximum with  $\perp$  light was

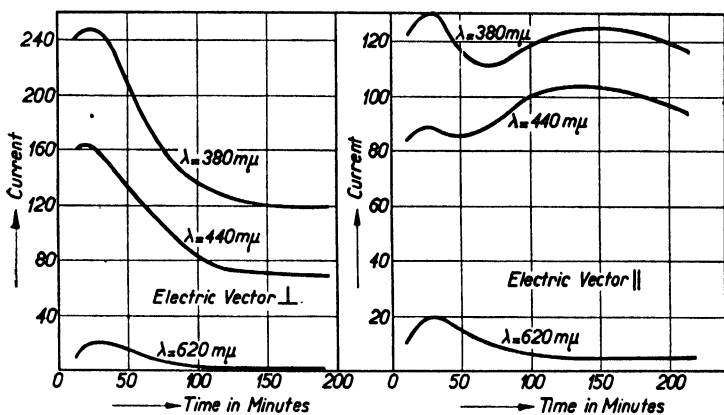


Fig. 52. Rubidium on platinum. Variation of photoelectric current with time of exposure (the time is not a linear scale for  $\theta$  here).

found, and must be ascribed to the maximum emission due to the normal photoeffect. In accordance with what we found to be true for thermionic emission, the maximum in this case indicates that the work function has reached its minimum value for the corresponding value of  $\theta$ .

The second maximum is connected entirely with the selective photoeffect. As we shall see in §§ 70 and 71, this selective photoeffect must be ascribed to a selective absorption of light. The selective absorption of light is much stronger at  $\lambda = 440 \text{ m}\mu$  and  $\lambda = 380 \text{ m}\mu$  than at longer wave-lengths, that is to say, the atoms which cause the selective absorption possess an absorption band in the neighbourhood of  $440\text{--}380 \text{ m}\mu$ .

Fig. 52 shows that the atoms which have this specific absorption for light are adsorbed mainly at values of  $\theta$  which are larger than those corresponding to the minimum work function.

The fact that this phenomenon was not observed in the adsorption of sodium on platinum is due to the circumstance that the absorption band lies at still shorter wave-lengths, and that

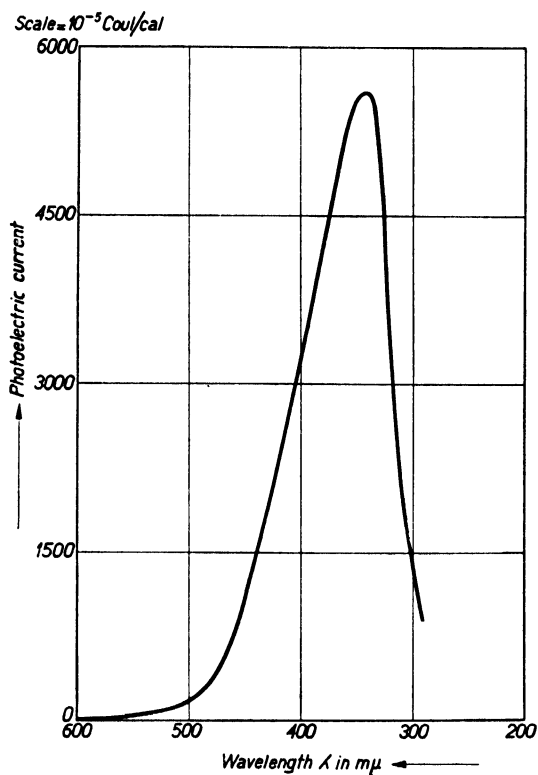


Fig. 53. Spectral distribution of photoelectric current; potassium on platinum. Electric vector of light ||. R. Suhrmann and H. Theissing, *Z. Phys.* 55, 708 (1929).

the source of light used for the measurements contained practically none of these wave-lengths. More recent work by Ives and Briggs\* shows that in the adsorption of sodium on silver and on tungsten such a maximum is present at  $\lambda = \sim 290$  m $\mu$ .

More especially has the work of Suhrmann and Theissing† shown that the existence of the selective photoeffect, as it is

\* H. E. Ives and H. B. Briggs, *Phys. Rev.* 38, 1488 (1931).

† R. Suhrmann and H. Theissing, *Z. Phys.* 55, 701 (1929).

indicated by large values of the ratio  $\parallel/\perp$ , is connected with a spectral maximum. Their measurements extend into shorter wave-lengths than those of Ives, and they come to the conclusion that in the adsorption of potassium on platinum at small values of  $\theta$  a normal sensitivity curve is found for  $\parallel$  light as well as for  $\perp$  light. At greater values of  $\theta$ , however, a selective effect is found and there is a maximum in the sensitivity curve for  $\parallel$  light in the ultraviolet at  $\lambda = 344 \text{ m}\mu$  (see Fig. 53).

From the above it may be concluded that measurements with  $\perp$  light and with light of relatively long wave-length give us information about the electrical double layer which is formed by the adsorption, and that measurements with  $\parallel$  light, especially at a large angle of incidence, and with light of sufficiently short wave-length so that it falls within the region of the selective absorption, give us information about the absorption of light by the absorbed atoms themselves.

#### § 41. The change of the photoelectric threshold.

During the building up of the adsorbed electropositive layer the photoelectric threshold is shifted from the value for the pure metal with no covering of adsorbed material to much longer wave-lengths. In accordance with the relatively high values of the work function the photoelectric threshold of the pure metals is usually relatively far in the ultraviolet (see § 7). The adsorption of the alkali metals brings about a shift into the visible, and in the cases of potassium, rubidium and caesium even into the infrared.\* When later a larger fraction of the surface becomes covered, the photoelectric threshold is shifted back again toward shorter wave-lengths over a certain distance. The behaviour here is thus similar to that in the case of the thermionic emission (see §§ 28 and 38). With increasing  $\theta$  the work function decreases, due to the fact that at first positive ions are adsorbed, and then atoms next to the ions. After passing a minimum the work function increases, since in the later stages of the adsorption process atoms are added which are so polarized that the dipole has its negative end directed away from the surface.

\* H. E. Ives, *Astrophys. J.* **60**, 209 (1924).



Ives and Olpin\* deduced from their measurements that the photoelectric thresholds which had undergone the greatest shifts toward the long wave-lengths in the adsorption of the various alkali and alkaline earth metals were identical with the first lines of the principal series of the adsorbed atoms, i.e. with their chief resonance lines. Thus the maximum excursion of the photoelectric threshold would be independent of the supporting metal, and would be given only by the resonance energy of the adsorbed atom. The values measured by Ives and Olpin are given in Table VII together with the wave-lengths of the chief resonance lines. If this correlation really existed it would indicate that the photoelectrons have their source in the adsorbed atoms at this stage of the adsorption process. These atoms would have to be brought into their first excited state (§ 11) by the absorption of light in order to emit an electron through collisions. We have already noted that at the values of  $\theta$  at which maximum photoemission is reached a large part of the emitted electrons may, to be sure, come from the adsorbed atoms, but that in the first place the absorption band of these atoms is at shorter wave-lengths, while the photoelectric emission at the threshold is given by the electrons of the supporting metal.

More recent experiments have shown that there is no correlation between the maximum excursions of the photoelectric thresholds and the resonance lines of the adsorbed atoms. Brady† found for the adsorption of potassium on silver that the photoelectric threshold was shifted from the value for pure silver,  $\lambda = 260 \text{ m}\mu$  to  $\lambda = 580 \text{ m}\mu$ , and that at larger values of  $\theta$  it was shifted back to  $\lambda = 550 \text{ m}\mu$  again. The work of Suhrmann and Deponte‡ shows that in the adsorption of barium on nickel there is a maximum excursion of about 2.6 volts which corresponds to a wave-length of  $475 \text{ m}\mu$ . Brady's values for the alkali metals and the value found by Suhrmann and Deponte are given in Table VII. It must be noted that in cases

\* H. E. Ives and A. R. Olpin, *Phys. Rev.* **34**, 117 (1929).

† J. J. Brady, *Phys. Rev.* **37**, 230 (1931); **39**, 546 (1932); **41**, 613 (1932).

‡ R. Suhrmann and R. Deponte, *Phys. Z.* **34**, 630 (1933); *Z. Phys.* **86**, 615 (1933).

where Ives and Olpin as well as Brady used silver as supporting metal, the former found a very much greater shift of the photoelectric threshold. It is, however, certain that the underlying layer of silver as prepared by Brady by slow evaporation is much more free of gas than that of Ives and Olpin. Suhrmann and Schallamach,\* who also used a very gas-free silver layer, found like Brady for the adsorption of potassium a maximum excursion of the threshold to  $\lambda = 580 \text{ m}\mu$ . The silver layer used by Ives and Olpin very probably contained some oxygen which would cause a greater shift of the photoelectric threshold. As a matter of fact it is very difficult to make a compact layer of silver free of oxygen, and we shall see in § 50 that in the adsorption of alkali metal ions on a surface covered with oxygen the work function is lowered more than in the absence of oxygen. Thus the maximum excursion of the photoelectric threshold proves to be dependent on the underlying layer.

Table VII

Adsorbed element	Wave-length of resonance line $\text{m}\mu$	Photoelectric threshold in maximum position on Ag, according to Ives and Olpin $\text{m}\mu$	Photoelectric threshold in maximum position on Ag, according to Brady. Ba on Ni according to Suhrmann and Deponte $\text{m}\mu$
Li	670.8	670	—
Na	589.6	590	—
K	789.9	770	580
Rb	794.7	795	620
Cs	894.3	895	660
Ba	791.1	790	475

#### § 42. Maximum excursion of the photoelectric threshold and the maximum of the photoelectric emission.

When the maximum shift of the photoelectric threshold is reached the work function is at a minimum. It is, therefore, very probable that when the fraction of the surface covered has reached the value  $\theta_m$  (§ 28) at which the work function is a minimum, the photoelectric threshold has been shifted as

\* R. Suhrmann and A. Schallamach, *Z. Phys.* **79**, 153 (1932).

far as possible toward longer wave-lengths. There are, however, no direct determinations of this. Suhrmann\* assumed that at the moment when the maximum excursion of the photoelectric threshold is reached a monatomic covering of the surface is also attained, and in his later work he defines such a layer as a fully occupied monatomic layer.† In Chap. III we have seen that at  $\theta_m$  the surface was far from completely covered with a monatomic layer, so that we may here also conclude that at the moment when the photoelectric threshold has reached its maximum excursion the monatomic layer is not yet complete ( $\theta_m$ ).

During the further building up of the adsorbed layer the photoelectric threshold is shifted back again, due to the atoms which are oppositely polarized (§ 28). The selective photoeffect which is due to just those atoms increases, and is even, as we shall see later, shifted toward longer wave-lengths (§ 70). Therefore in the measurement of photoelectric emission with light in which a sufficient number of those wave-lengths occur to which the surface is selectively sensitive, the photoeffect will continue to increase when  $\theta_m$  is exceeded. If the selective region is situated at sufficiently long wave-lengths this result will be already obtained by measurements with white light. Thus Brady‡ found, in his measurements with potassium, rubidium and caesium on silver, that after passing the minimum values of the thresholds at 580, 620 and 660  $m\mu$  respectively, these limits returned to 550, 590 and 630  $m\mu$  respectively, but that the total photoemission continued to increase, to reach a maximum at values of  $\theta$  which were respectively 4.1, 3.3 and 3.6 times as great as the values of  $\theta_m$ , and then to decrease again. Brady reached the further conclusion that even at the greatest excursion of the photoelectric threshold the thickness of the adsorbed layer was more than monatomic. Since, however, he had no idea of the actual specific surface of the silver layer obtained by evaporation, and since such surfaces are usually much larger than the ap-

\* R. Suhrmann and H. Theissing, *Z. Phys.* **55**, 701 (1929).

† R. Suhrmann, *Z. Elektrochem.* **37**, 682 (1931).

‡ J. J. Brady, *Phys. Rev.* **41**, 613 (1932).

parent surface, one must not for the time being attach too much importance to his absolute values. Moreover, it must be noted that Brady's measurements were made at a very low temperature ( $-180^{\circ}\text{C.}$ ) of the silver surface, which would make the surface migration, even of caesium at larger values of  $\theta$ , minimal. Because of this fact his absolute values are those whereby practically every incident atom remains adsorbed as ion or atom at the spot where it first struck the surface. This does not give the most favourable distribution. If this is not taken into account one might be inclined to ascribe the maxi-

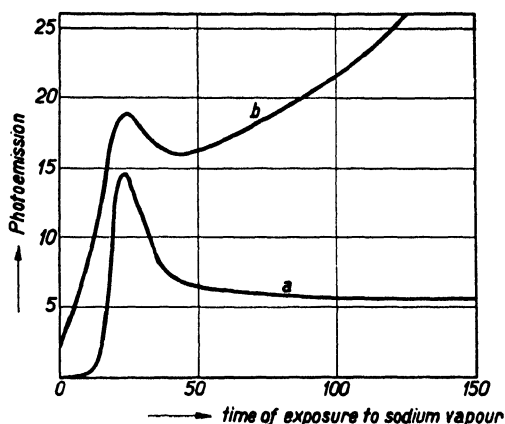


Fig. 54. Photoemission of sodium on tungsten as a function of the amount of adsorbed ions and atoms. Curve *a*: photoemission in white light, wave-length  $>3500\text{ \AA}$ . Curve *b*: photoemission in ultraviolet light of wave-length  $2537\text{ \AA}$ .

imum total emission in Brady's experiments to the approximately completely filled monatomic layer. This inclination is supported by the fact that if about twice as many alkali metal atoms are evaporated on the surface, the properties of the layer become those of the alkali metals in bulk, which might well be the case if the layer were two atoms thick. If this assumption is correct,  $\theta_m$  would be reached for potassium, rubidium and caesium on silver at respectively 24, 30 and 28 per cent.

If the selective photoeffect is situated somewhat more toward shorter wave-lengths, by measurements with long-wave light a maximum of the emission is reached at the moment when the photoelectric threshold has reached its

maximum excursion, while by measurements with short-wave light the maximum is reached later, or, as in the observations by Ives of rubidium on platinum (cf. § 40), two maxima are found.

Fig. 54 represents the photoelectric emission for the adsorption of sodium on tungsten. In this case the spectral region in which the selective emission of the adsorbed atoms is excited lies so far in the ultraviolet, that on illumination with white light ( $\lambda > 3500 \text{ \AA.}$ ) one obtains practically only the emission of the conduction electrons of the tungsten metal. The curve (curve *a* in Fig. 54) rises according to an *e* function, reaches a maximum, and falls again to a constant value. Upon illumination with ultraviolet light ( $\lambda = 2537 \text{ \AA.}$ , curve *b*) one measures a photoeffect without the adsorption of any sodium, since tungsten itself has an emission for this light. The curve then rises with increasing amount of adsorbed sodium, reaches a maximum at the same moment as curve *a*, then passes through a minimum to rise again, since at this point the selective emission dominates.\*

### § 43. The source of the photoelectrons.

As has already been stated several times (§§ 40 and 42), the source of the photoelectrons when small fractions of the surface are covered by an adsorbed layer is in the supporting metal, while at greater values of  $\theta$  a selective photoeffect begins to be dominating, whereby the photoelectrons originate in the adsorbed atoms. In order to measure the selective effect the electric vector of the light must have a component perpendicular to the surface, and moreover the light used for the measurements must lie within the absorption band of the adsorbed atoms (see also § 40).

It may be expected that as long as only ions are adsorbed on the surface, i.e. at small values of  $\theta$ , there can be no selective photoeffect, and that it will begin to be appreciable as soon as some atoms are also adsorbed. In the discussion of the thermionic emission of tungsten upon which caesium or

\* J. H. de Boer and C. F. Veenemans, will appear shortly in *Physica*, 2 (1935).

barium is adsorbed it was seen that the work function underwent about 0.4 of its total lowering due to the pure ion adsorption (§§ 28 and 32). On the basis of this we may expect that the selective photoeffect will only begin to be manifested when the concentration on the surface has become so large that the excursion of the photoelectric threshold has reached more than 0.4 (measured in terms of energy) of its total excursion.

Very accurate and elegant experiments by Ives and Briggs\* and also by Suhrmann and Schallamach† have shown that this is actually the case. In these experiments use is made of the accurately known optical constants of the supporting metal. Ives‡ had already shown that when there is a selective effect, the photoeffect at every wave-length is proportional to the intensity of the electric vector of the light used for the measurements just above the surface of the supporting metal. Silver is especially suitable for such experiments, as it has a sharp transmission band for ultraviolet light at 3160 Å. Consequently not only the intensity of the electric vector of the light just above the surface, but also the absorbed light just inside the metal vary in a very characteristic manner with the wave-length. When a film of sodium is deposited on silver, and just enough so that the maximum excursion of the photoelectric threshold is reached, it appears that in the range of wave-lengths between 3000 and 3600 Å. the photoemission as a function of the wave-length is given by the energy density of the light just above the surface.§ This light is absorbed by the sodium atoms and it causes photoelectrons to escape from these atoms.

At very small values of  $\theta$ , however, the spectral distribution of the photoemission in this same range of wave-lengths was found to be given by the absorption of light just inside the silver. It is thus shown in a very nice manner that the electrons in this case originate in the silver. It was now shown that at

\* H. E. Ives and H. B. Briggs, *Phys. Rev.* **40**, 802 (1932).

† R. Suhrmann and A. Schallamach, *Z. Phys.* **79**, 153 (1932).

‡ H. E. Ives, *Phys. Rev.* **38**, 1209 (1931).

§ H. E. Ives and H. B. Briggs, *Phys. Rev.* **38**, 1477 (1931).

a  $\theta$  value such that the photoelectric threshold is at about 4000 Å. practically all the electrons still originate in the silver, but that a slight influence of the adsorbed atoms becomes appreciable. While the photoelectric threshold of silver, when  $\theta=0$ , is at  $\lambda=2800$  Å. (4.7 electron volts) and its maximum excursion is reached at  $\lambda=5900$  Å. (2.1 electron volts), at  $\lambda=4000$  Å. (3.1 electron volts) 60 per cent. of the total lowering of the work function is attained, so that on the basis of our views at the beginning of this section an appreciable number of atoms must already be present. In the adsorption of caesium on silver and platinum similar results were obtained; the results were only slightly less satisfactory because the maximum of the selective emission for caesium occurs within this range, so that the curves were distorted. In the case of sodium, as we saw in § 40, the maximum lies somewhat more toward the ultraviolet, at  $\lambda=2900$  Å. As has already expressly been stated, even at greater values of  $\theta$  when wave-lengths are used which correspond to the region of the photoelectric threshold, the photoelectrons originate in the supporting metal.

**§ 44. The change of the photoemission with temperature in the adsorption of electropositive atoms.**

An important indication of the presence of adsorbed ions or atoms on a metal surface is the behaviour of the photoemission upon change of cathode temperature. As we have seen in § 6 the photoemission increases with increase of temperature within the high-temperature range. In the range of lower temperatures the photoemission is hardly dependent on the temperature at all, at least in experiments with pure metal surfaces.\* The behaviour of surfaces which show a selective photoeffect, or which have their work function lowered by the presence of a dipole layer, is quite different. The influence of temperature on the selective photoeffect is such that it may in general be said that the emission decreases with increasing temperature. We shall now examine the changes brought about by temperature in the dipole layer.

\* Cf. A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, pp. 87 ff. (1932).

In the region of small values of  $\theta$  in which only positive ions are adsorbed on the surface, an increase of temperature will cause an increase of the dipole moment. Upon increase of temperature the ions will on the average be somewhat farther away from the surface, so that the active length of dipole is directly increased, while in addition the polarization of the positive ion, which is the cause of a small, oppositely acting dipole (§ 27), will be decreased. An increase of the dipole moment causes a greater lowering of the work function, so that it may be expected that an increase of temperature will cause an increase of the photoemission.

The influence of a rise in temperature on the adsorbed atoms will be quite different. The dipole of these atoms is induced mainly by the charge of the positive ions. It must therefore be expected that an increase of temperature will be followed by a decrease of these induced moments, since the polarization decreases not only because of the increase of the average distance of the adsorbed ions and atoms from the surface, but also because of the increase in the separation between ions and atoms on the surface. From this cause the work function will thus increase upon increase of temperature. Whether upon increase of temperature a decrease or an increase of the photoeffect will be found at larger values of  $\theta$ , and especially for those values of  $\theta$  for which the maximum lowering of the work function occurs ( $\theta_m$ ), depends upon whether or not the decrease of the induced dipoles in the atoms is able to compensate for the increase of the active moment of the ions. In any case it must be expected that the increase of the photoeffect with temperature at small values of  $\theta$  when only ions are present will be greater than at greater values of  $\theta$  when atoms are also present.

Suhrmann and Theissing\* examined the photoemission of a polished platinum surface covered with a very small amount of sodium at room temperature (293° abs.) and at the temperature of liquid air (83° abs.). The photoelectric threshold of this system was still within the ultraviolet (349 m $\mu$ ), thus  $\theta$  was still much below the value of  $\theta_m$ . At 83° abs. the photocurrent was actually smaller than at 293° abs., while at the

\* R. Suhrmann and H. Theissing, *Z. Phys.* **73**, 709 (1932).



lower temperature the photoelectric threshold lay toward shorter wave-lengths (Fig. 55). In this case therefore an increase of temperature really does give a decrease in the work function. This was true for all measurements with wave-lengths lying between the photoelectric threshold and  $\lambda = 260 \text{ m}\mu$ . For shorter wave-lengths the temperature effect was just the opposite, and a decrease of the temperature was

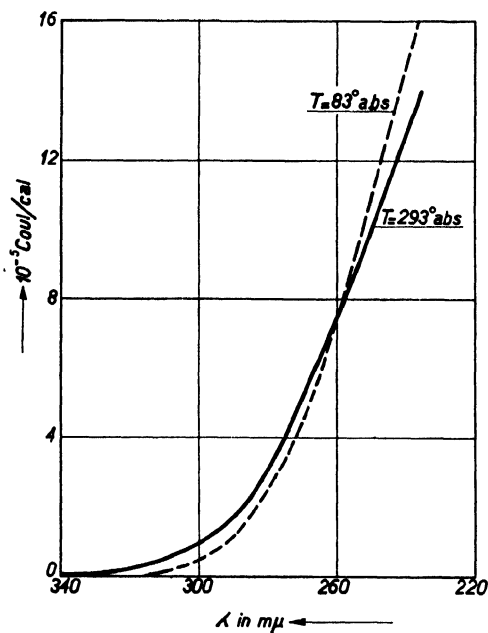


Fig. 55. Effect of temperature on the photoelectric emission of a platinum cathode with a few sodium ions on it, according to R. Suhrmann and H. Theissing, *Z. Phys.* 73, 717 (1932).

followed by an increase of the emission. This effect must perhaps be ascribed to the selective photoeffect, because even at this fraction of the surface covered there are probably already a certain number of atoms present whose emission is relatively far in the ultraviolet (see §§ 42 and 70).

Suhrmann and Theissing also measured the influence of temperature when sodium atoms were adsorbed on platinum black which was deposited on silver. This surface must be considered as quite different from that of polished platinum, so that the magnitude of the effects may not be compared with

those found with polished platinum. They took measurements with this surface at two different values of  $\theta$ : the first at  $\theta < \theta_m$  and the other at such a value of  $\theta$  at which the selective effect was clearly present. As the photoelectric threshold lay farther toward the red in the second than in the first case, the  $\theta$  value in the second case was closer to  $\theta_m$ . The result was that in the first case the increase of temperature from  $83^\circ$  abs. to  $293^\circ$  abs. caused a very considerable increase of the photocurrent and a decrease of the work function ( $\Delta\phi = 0.38$  volt).

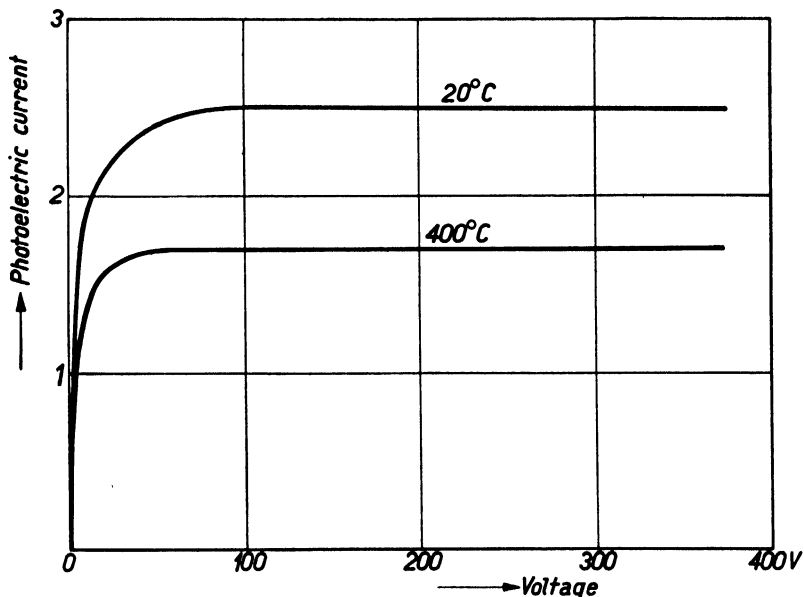


Fig. 56. Photoelectric current of a barium-covered nickel cathode upon illumination with a tungsten-band lamp, according to R. Suhrmann and R. Deponete, *Z. Phys.* **86**, 625 (1933).

In the second case where  $\theta$  was close to  $\theta_m$  the influence of the temperature was in the same sense but much less strong, as we expected on the basis of our conception. At shorter wavelengths an increase of temperature gave a decrease of photocurrent because of the temperature influence on the selective effect.

Suhrmann and Deponete\* examined the influence of temperature on the photoemission of layers of barium adsorbed on nickel. No temperature effect was found with a thick

\* R. Suhrmann and R. Deponete, *Z. Phys.* **86**, 615 (1933).

visible layer of barium deposited on nickel between 100 and 400° C. Thin layers of adsorbed barium, however, whose  $\theta$  value is such that the minimum work function is attained (the three layers examined had work functions of 2.62, 2.66 and 2.86 volts respectively), showed clearly a decrease in photocurrent upon increase of temperature between 20 and 500° C., as appears in Fig. 56 where the photocurrent is given as a function of the tension between cathode and anode for 20 and 400° C. In this case (barium on nickel,  $\theta \sim \theta_m$ ), the decrease in the dipole of the atoms upon increase of temperature seems

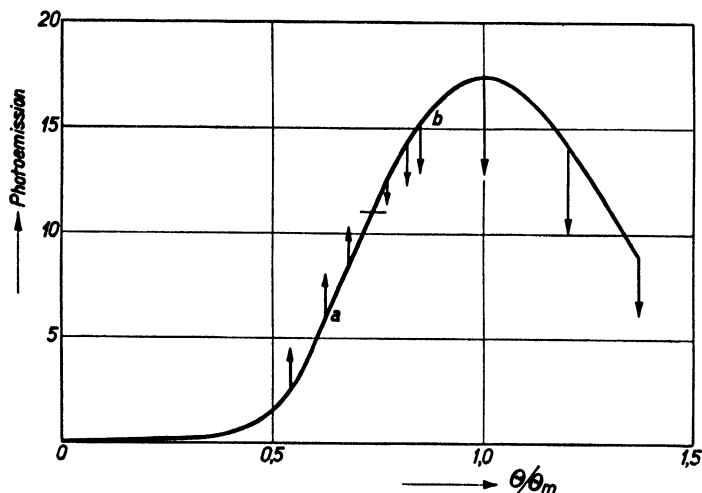


Fig. 57. Effect of temperature on the photoelectric emission of sodium on tungsten. ↑, emission is raised with increasing temperature. ↓, emission is lowered with increasing temperature. Lengths of arrows show the magnitude of the temperature effect.

to be more important than the increase of the dipoles of the ions. The work function, which was determined by Suhrmann and Deponce by means of the method of the complete photoelectric emission described in § 7, changed in one case from  $\phi = 2.654$  volts at 20° C. to 2.703 volts at 400° C.

Compensation of the influence due to the ions by that due to the atoms was also found in the case of sodium on tungsten.\* If during the formation of the layer the temperature influence is examined at various intervals, it appears that at small values of  $\theta$ , at which the photoemission is still much smaller than its

\* J. H. de Boer and C. F. Veenemans, will appear shortly in *Physica*, 2 (1935).

maximum value, an increase of temperature from room temperature to about  $80^{\circ}\text{C}$ . causes an increase of the photoemission (see Fig. 57), while at greater values of  $\theta$  the temperature effect is just the opposite. Between the two  $\theta$  ranges there is a point on the curve where the temperature effect is by chance equal to zero. This is the point where the increase in the dipole of the ions is exactly compensated for by the decrease in the induced dipole of the atoms. The temperature effect is

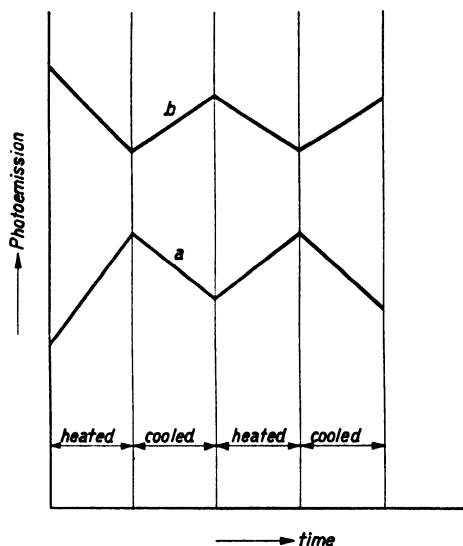


Fig. 58. Variation of photoemission, when temperature of the sodium-covered tungsten cathode is raised and lowered. *a* and *b* correspond to *a* and *b* of Fig. 57. The first change is greatest, due to migration effect.

easily reproducible and is reversible in all parts of the curve. There is, however, at many values of  $\theta$  an irreversible change upon the first heating of the surface, which is represented in Fig. 58 where the temperature effect of the points *a* and *b* of Fig. 57 is given in more detail. This first irreversible change must be ascribed to the fact that in the sublimation all the atoms do not have sufficient kinetic energy (the sublimation takes place at room temperature, while the tungsten surface is also cold) to find their most favourable positions by means of surface migration. Upon the first heating of the surface the atoms find their most favourable positions, which they then retain.

## CHAPTER VI

### DOUBLE LAYERS FORMED BY THE ADSORPTION OF GASES

#### § 45. Introduction: metals and gases.

We have already seen that gases such as the halogens and oxygen may be expected to be adsorbed on metal surfaces as negative ions (§ 21). In such a case we must expect that the work function in thermionic emission and the photoelectric threshold will be raised to a considerable extent, since an electric double layer is formed with its negative side away from the surface. This phenomenon is actually observed, and in the literature on thermionic emission\* as well as that on photoelectric emission† many examples can be found of a decrease in the electron emission due to the adsorption of oxygen. This phenomenon is often spoken of as photoelectric fatigue.

In general gases have a great influence on thermionic emission as well as on photoemission, so great in fact that it was sometimes maintained that the presence of a gas was essential for electron emission. Experiments, especially those of Langmuir,‡ have shown that this is not true, but that films of gas can strongly influence the electron emission of pure metals.

Practically every metal is covered with a surface oxide film after exposure to air, even metals like platinum and gold. In very many cases this fact can be ascertained by carrying out experiments which are concerned specifically with the surface of the metal; thus mercury will wet surfaces of tungsten or zirconium which have been formed by evaporation in a high

\* Cf. W. Schottky and H. Rothe, *Handbuch der Experimentalphysik*, 13, 2, pp. 204–10 (1928); O. W. Richardson, *The Emission of Electricity from Hot Bodies* (1921).

† Cf. B. Gudden, *Lichtelektrische Erscheinungen*, pp. 54 ff. (1928); A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, pp. 48 ff. (1932).

‡ I. Langmuir, *Phys. Z.* 15, 516 (1914); *J. Amer. chem. Soc.* 38, 2221 (1916).

vacuum, while the wetting is much more difficult when the surfaces have been exposed to the air for a short time. Zirconium crystals which have been formed in a completely oxygen-free atmosphere are rapidly attacked by iodine under application of heat. If, however, these crystals have been previously exposed to air for a short time, the reaction with iodine proceeds much more slowly.\* Whalley and Rideal† showed how difficult it is to keep a gold surface really oxygen-free by the method described in § 18, in which the potential difference in a conducting gas atmosphere is measured. An oxygen-free gold surface was found to be 1.56 volts more negative than a gold surface on which oxygen was adsorbed. This means that the electric double layer on the gold surface covered with oxygen causes a potential jump of 1.56 volts, and is indeed so formed that its negative part is on the outside.

An investigation by Cassel and Glückauf‡ gives an example of the difficulty of freeing platinum of an adsorbed film of oxygen. They did not succeed in removing the oxygen by heating in a high vacuum. Platinum is one of the most difficult metals to outgas, while tungsten can more easily be outgassed by heating in a high vacuum, since practically all compounds of tungsten are more volatile than the metal itself.

The behaviour of hydrogen with respect to metals is in most cases just the opposite to that of oxygen. Hydrogen usually forms positive ions on the metal surface (see also § 21) and thus causes an electric double layer which reduces the work function and shifts the photoelectric threshold toward longer wavelengths. As was shown by Bowden§ the behaviour of hydrogen and oxygen at the electrodes in electrochemical processes is in complete agreement with the above.

It may be found remarkable that hydrogen, in spite of its high ionization tension (13.54 volts), is nevertheless able to form positive ions on a metal. Franck|| pointed out that the

\* J. H. de Boer and J. D. Fast, *Z. anorg. Chem.* **187**, 195 (1930).

† H. K. Whalley and E. K. Rideal, *Proc. roy. Soc. A*, **140**, 484 (1933).

‡ H. Cassel and E. Glückauf, *Z. phys. Chem. B*, **18**, 347 (1932).

§ F. P. Bowden, *Proc. roy. Soc. A*, **125**, 446 (1929).

|| J. Franck, *Nachr. Ges. Wiss. Göttingen*, p. 293 (1933).

gain in energy by the taking up of a positive hydrogen ion *within* the metal (and this is valid to a certain extent for adsorption on the surface) is very large because of the fact that the very mobile electrons within the metal form so to speak a swarm about the positive ion, which is thus more strongly bound.\* A positive ion has in this respect an advantage over a negative ion, since the formation of a corresponding swarm of positively charged components about a negative ion is impossible. Thus because of the fact that in the metal the components carrying the negative charge are small and mobile, while the components carrying the positive charge are large and fixed in definite positions, positive ions are more strongly bound than negative ions.

When electronegative atoms are transformed into negative ions on the surface we may imagine that opposite the spot at

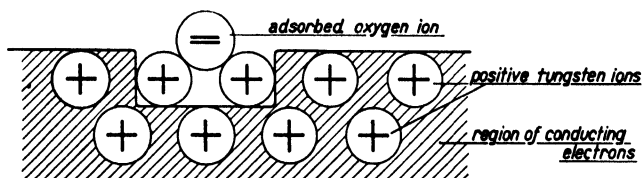


Fig. 59. Diagram representing the adsorption of oxygen on tungsten.

which the negative ion is adsorbed there are no conduction electrons, or at least fewer conduction electrons on the average than occur normally. The adsorbed negative ions thus stand opposite the positive metal ions of the surface, while at a distance of one atom diameter deeper into the metal the normal structure of the metal begins, as represented very schematically by Fig. 59 which gives the adsorption of oxygen on tungsten. In this diagram the positive metal ions are assumed to be singly charged; a higher charge on these ions would lead of course to a similar picture. According to this representation we are now concerned with an oxide molecule on the surface which is, however, completely incorporated in the metal. Such a surface oxide molecule must not be conceived as an indissociable whole; the oxygen atoms can, for example, at suffi-

\* Cf. also K. F. Herzfeld and M. Goeppert-Meyer, *Z. phys. Chem. B*, 26, 203 (1934).

ciently high temperatures exhibit the phenomenon of surface migration, or they may evaporate as oxygen atoms without carrying any metal atoms along, as a normal oxide can dissociate into its atoms upon heating.

In the adsorption of positive ions on a metal surface there is a surplus of electrons present opposite the spot where the ion is adsorbed. These electrons are not necessarily bound to definite positions. Thus there are no negative ions in the metal opposite the adsorbed positive ion, but an electron distribution whose action at a sufficiently great distance from the surface can be described, as we have already seen, as that of an image charge.

In the process of outgassing metals the various gases diffuse to the surface and are more or less easily liberated from the surface. Metals like platinum and the other metals of the platinum group, as well as iron and nickel, often contain considerable quantities of hydrogen, while hydrogen also diffuses readily through these metals. Oxygen is easily taken up by copper and silver; nickel takes up carbon monoxide very well, and water vapour can diffuse through gold or copper.\* We must limit our choice in this chapter and treat only a few examples in more detail.

#### § 46. Oxygen on tungsten.

When oxygen molecules come into contact with a cold tungsten surface we may assume that the molecules will be adsorbed as such. At higher temperatures the molecules will, however, probably dissociate into atoms which will be adsorbed, and the adsorption will take place in the form of negative ions (see §§ 21 and 45). This dissociation of the molecule on the surface is apparently entirely analogous to the similar phenomenon in the adsorption of hydrogen which we mentioned in § 21. When tungsten is heated to a high temperature in an atmosphere of oxygen, molecules of  $\text{WO}_3$  are formed which then evaporate. If, however, a tungsten filament is heated to above  $1300^\circ \text{K.}$  in oxygen at a very low pressure

\* J. H. de Boer and J. D. Fast, will appear shortly in *Rec. Trav. chim. Pays-Bas* (1935).



( $\sim 10^{-3}$  mm.), an adsorbed layer of oxygen ions is formed which strongly reduces the electron emission.\* The thermionic emission has been measured by Kingdon,† who compensated for the removal of oxygen by the evaporating  $\text{WO}_3$  by a continual addition of oxygen (from a mixture of  $\text{BaO}_2$  and  $\text{KMnO}_4$  at  $160^\circ \text{C}.$ ). His measurements gave, independent of the gas pressure used ( $0.2\text{--}1 \times 10^{-3}$  mm. Hg), a work function of 9.2 volts, and a value of  $A$  in Richardson's formula (§ 4) of  $5 \times 10^{11}$  amp./cm.<sup>2</sup> deg.<sup>2</sup> These values must thus be considered as those for a tungsten surface which is covered as far as possible with oxygen.

Langmuir and Villars‡ studied the evaporation of oxygen from a surface. It is appreciable only above  $1500^\circ \text{K}.$ , while it proceeds very rapidly above  $2000^\circ \text{K}.$  From the temperature coefficient of the evaporation the heat of evaporation was found to be 162 kg. cal. per gram atom, which value refers to the evaporation in the form of atoms and is much larger than the energy of dissociation of an oxygen molecule into atoms. This value holds for relatively small values of  $\theta$ , the fraction of the surface covered with adsorbed material, thus for the state when relatively little oxygen is adsorbed. When more oxygen is adsorbed the evaporation energy is smaller.

Becker§ also found that the rate of evaporation of adsorbed oxygen increases very rapidly with the surface concentration. He found in addition that at  $1400^\circ \text{K}.$ , at which temperature there is as yet no evaporation, a very rapid surface migration could be observed (§ 36).

Just as in the adsorption of electropositive atoms (positive ions), the work function, and consequently in the first approximation also the logarithm of the electron emission, changes linearly with  $\theta$ , so in the adsorption of oxygen the logarithm of the electron emission in the region of small values of  $\theta$  decreases linearly with the quantity adsorbed (Fig. 60).

\* Cf. I. Langmuir, *Industr. Engng Chem.* **22**, 390 (1930); Nobel Lecture, *Chem. Rev.* **13**, 147 (1933); *Angew. Chem.* **46**, 720 (1933).

† K. H. Kingdon, *Phys. Rev.* **24**, 510 (1924).

‡ I. Langmuir and D. S. Villars, *J. Amer. chem. Soc.* **53**, 486 (1931).

§ J. A. Becker, *Trans. Faraday Soc.* **28**, 157 (1932).

Molecular nitrogen has no effect on the thermionic emission of tungsten. A discharge in nitrogen which gives rise to nitrogen ions,  $N_2^+$  ions for example, causes a decrease of the electron emission. This phenomenon was at first thought to be due to the formation of a film of adsorbed nitrogen.\* Langmuir† discovered later, however, that this decrease of the electron emission also must be ascribed to the formation of a surface oxide film. The active nitrogen decomposes adsorbed water vapour or metallic oxides which are present on the walls of

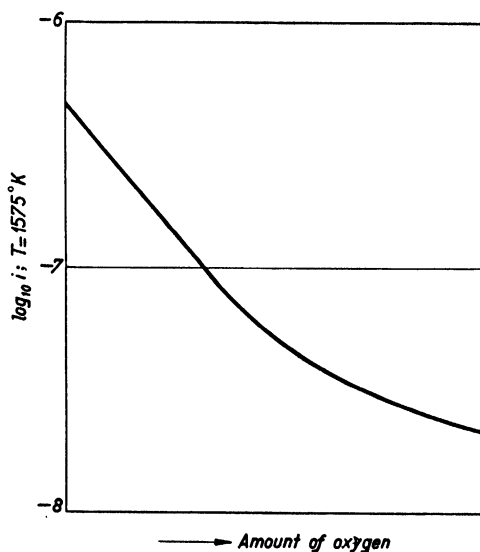


Fig. 60. Variation of logarithm of electron emission with the amount of oxygen adsorbed on the surface. J. A. Becker, *Trans. Faraday Soc.* **28**, 157 (1932).

the tube and the surfaces of the electrodes. Hereby oxygen is generated, probably in atomic form, which reacts with the surface of the tungsten filament and gives a surface oxide film. When there is absolutely no oxygen present active nitrogen does not cause the formation of an adsorbed film which would alter the electron emission, but it is even able to remove an oxide film already present.

Metastable neon atoms can also free oxygen atoms by striking the walls of the discharge tube.

\* I. Langmuir, *Phys. Rev.* **2**, 460 (1913); *Phys. Z.* **15**, 516 (1914).

† I. Langmuir, *Phys. Rev.* **37**, 1006 (1931).

### § 47. Oxygen on other metals.

The adsorption of oxygen on platinum also causes a strong increase in the work function. Cassel and Glückauf\* found the work function of a platinum surface covered with oxygen to be 8.46 volts. Neither by long heating—whereby the evaporation of platinum was appreciable, but the oxide layer still remained, probably because oxygen existed within the filament itself—nor by treatment with mercury vapour were they able to remove this oxide film. By heating in an atmosphere of hydrogen the oxide film was removed and replaced by an adsorbed hydrogen film, so that low values of the work function were obtained. Heating of the filament in a high vacuum at this point causes the work function to increase and to pass over to that of the pure metal. The work function of pure platinum is very high (DuBridge 6.2, Langmuir 6.62, Cassel and Glückauf 6.45), and the high value of  $A$  in the Richardson formula is very striking. As we have already seen in § 4 the value of  $A$  for pure metals is 120. Very high values are found for pure platinum,  $4 \times 10^7$  for example (Cassel and Glückauf). DuBridge,† who also outgassed very rigorously, still found for  $A$  a value of 17,000. In § 8 we saw that the value of the work function is greater according as the distance between the atoms in the metal is smaller, thus according as the radius of the metal atoms is smaller. Now an atom of platinum is just about the same size as an atom of tungsten, but the work function of platinum is much higher than that of tungsten, so that the parallelism between these two quantities does not hold in this case. It must be noted that Suhrmann,‡ working with outgassed platinum foils, found a constant value of the work function of 4.45 volts, a value that differs very little from that of tungsten, while at the same time a normal  $A$  value of about 100 was found.

Metals such as zirconium and hafnium, as soon as they have been exposed to the air, possess a surface oxide film (§ 45) which is very difficult to remove. Upon heating to very high

\* H. Cassel and E. Glückauf, *Z. phys. Chem. B*, **18**, 347 (1932).

† L. A. DuBridge, *Phys. Rev.* **32**, 961 (1928).

‡ R. Suhrmann, *Z. phys. Chem.* **13**, 18 (1923).

temperatures the oxide film slowly disappears, and the oxygen is taken up in the metal lattice.\* As was also the case with thorium the oxygen takes up its position between the normal components of the lattice, and thus changes very appreciably the electrical resistance, the melting point and also the lattice constant.†

When by long heating of a zirconium or hafnium filament the surface oxide film gradually disappears, the work function decreases, and at the same time the value of  $A$  in Richardson's formula decreases. Zwikker‡ found with normal, that is to say oxygen-covered, zirconium filaments,  $A = 37,200$  and  $\phi_0 = 5.2$  volts, while after long heating  $A = 330$  and  $\phi_0 = 4.12$  volts were reached. For hafnium the values were  $A = 55,000$  and  $\phi_0 = 5.1$  volts before, and  $A = 14.5$  and  $\phi_0 = 3.53$  volts after long heating.

In photoelectric experiments it has been ascertained repeatedly that the photoelectric threshold is shifted toward shorter wave-lengths by the adsorption of oxygen. This has been found to be true for silver, gold, nickel, palladium, platinum and rhodium.§ In an investigation of the photoelectric properties of aluminium and several aluminium alloys Gerding|| found a large shift of the photoelectric threshold toward shorter wave-lengths when the metal surface, previously scraped clean in a vacuum, was exposed to the air. In the case of aluminium the photoelectric threshold was shifted from 5460 to 3400 Å., and in the case of an aluminium alloy containing 0.26 per cent. of mercury the threshold was shifted from 6125 to 3650 Å.

#### § 48. The influence of hydrogen.

In § 45 it was stated that the adsorption of hydrogen brings about a lowering of the work function because of the fact that

\* J. H. de Boer and J. D. Fast, *Z. anorg. Chem.* **187**, 187 (1930); J. H. de Boer, *Footnote-Prints rare Met.* **3**, 18 (1930).

† W. G. Burgers and J. A. M. van Liempt, *Z. anorg. Chem.* **193**, 158 (1930).

‡ C. Zwikker, *Proc. Roy. Acad. Amst.* **29**, 792 (1926); *Phys. Z.* **30**, 578 (1929).

§ Cf. for example, L. A. Welo, *Phys. Rev.* **12**, 257 (1918); E. H. Dixon, *Phys. Rev.* **37**, 60 (1931).

|| H. Gerding, *Z. phys. Chem. B*, **11**, 1 (1930).

the hydrogen is at least partially adsorbed in the form of positive ions. The lowering of the work function of platinum by hydrogen in the study of thermionic as well as photoelectric emission has long been known. Wilson\* obtained a lowering of the work function of as much as 2.2 volts by heating platinum in hydrogen. Since platinum in very many cases already contains a large amount of hydrogen, when this metal is outgassed one obtains an adsorption of hydrogen as positive ions on the surface due to the diffusion of the hydrogen from within the metal to the surface.† As in the well-known experiments on the adsorption of thorium on tungsten (§ 37), in this case the adsorbed ions and atoms come originally from within the metal. There is, however, a difference in the diffusion: hydrogen diffuses probably in the form of positive ions through the metal lattice, thorium diffuses along the crystal planes, or perhaps even mainly along the ribs (§ 34). During the outgassing of platinum Suhrmann‡ found that the photoelectric threshold which had previously lain at 2600 Å. was first shifted toward longer wave-lengths as far as 3000 Å. and then back again to 2700 Å., where it remained constant. As was stated in § 47 later investigators found that this last value does not represent the constant final value, but that it lies much farther in the ultraviolet, viz. at 1962 Å. (6.30 volts). If platinum is heated in hydrogen, hydrogen ions are taken up within the metal and on the surface, so that the electrical resistance falls sharply,§ and the photoemission as well as the thermionic emission increases. During the following outgassing the electrical resistance rises and the electron emission decreases. With metals like zirconium, hafnium and thorium, which as was stated in § 47 are able to take up oxygen in the lattice, this taking up of oxygen has just the opposite effect of that exhibited upon the taking up of hydrogen by platinum. The resistance is raised by the taking up of oxygen, while as we know

\* H. A. Wilson, *Phil. Trans. A*, **208**, 251 (1908).

† Cf. for example R. Suhrmann, *Z. anorg. Chem.* **203**, 241 (1931).

‡ R. Suhrmann, *Ann. Phys., Lpz.*, **67**, 43 (1922).

§ R. Suhrmann, *Z. Phys.* **19**, 1 (1923); K. Herrmann, *Ann. Phys., Lpz.*, **77**, 503 (1925).

the electron emission is lowered by the adsorption of oxygen, which is also contrary to the action of hydrogen. Thus negative oxygen ions within the metal as well as on the surface of the metal have an opposite influence to that of positive hydrogen ions.

The phenomenon described above in the case of platinum, where during outgassing the photoelectric threshold is first shifted toward longer wave-lengths and then by continued outgassing is shifted back to shorter wave-lengths, has been observed with many other metals, e.g. gold,\* rhodium† and silver.‡ In many of these cases the photoelectric threshold in the beginning before the outgassing is at a shorter wave-length than the final value for the pure metal. For example, the value for silver was about 2000 Å. at the start, the greatest shift to the red was to 3300 Å., and the final value was 2700 Å. The starting value is probably determined by an adsorption of oxygen, and the greatest shift toward the red by an adsorption of hydrogen. A surface of pure silver which has been entirely freed of gas by electronic bombardment has, according to the investigations of Suhrmann,§ its photoelectric threshold at 2600 Å., while charging the surface with hydrogen causes a shift to 3700 Å.

Finally it must be noted that hydrogen either causes no change in the photoelectric emission of the alkali metals or it causes a decrease, when for example hydrogen reacts upon potassium which is adsorbed on platinum.|| Hydrogen does not react with alkali metals to give positive but to give negative ions, since hydrides may be formed. Therefore we must actually expect a lowering of the photoemission. We shall see later that the adsorption of potassium atoms on such hydrides produces a strong selective photoemission (§ 66). The well-known sensitization of potassium cells by hydrogen is based upon this phenomenon.

\* L. W. Morris, *Phys. Rev.* **37**, 1263 (1931).

† E. H. Dixon, *Phys. Rev.* **37**, 60 (1931).

‡ R. P. Winch, *Phys. Rev.* **37**, 1269 (1931).

§ R. Suhrmann, *Z. Elektrochem.* **35**, 681 (1929); R. Suhrmann and A. Schallamach, *Z. Phys.* **79**, 156 (1932).

|| R. Suhrmann and H. Theissing, *Z. Phys.* **52**, 453 (1928).

§ 49. Changes in the value of  $A$  in Richardson's formula; relation between  $A$  and  $\phi$ .

While the value of  $A$  in Richardson's formula

$$i = AT^2 e^{\frac{-\epsilon\phi_0}{kT}}$$

is 120 for pure metals (§ 4), this value is quite different when electrical double layers are present. In the case of double layers whose positive side is away from the surface and which lower the work function, the value of  $A$  is usually very much lowered (see for example § 38), while with double layers which raise the work function a very much higher value of  $A$  is usually found (§§ 46 and 47). Thus in the adsorption of caesium on tungsten the value of  $A$  is reduced to 3.26, while the adsorption of oxygen brings about an increase of  $A$  to  $5 \times 10^{11}$ .

One might in the first instance expect a lowering in the value of  $A$  in all cases of adsorption on the surface, since the progress of the electron through the double layer is only accompanied by a gradually changing potential when the electron chooses its path between the ions of the double layer. If it exactly collides with an ion then the potential becomes infinitely great. If the electron passes close to an ion there will be a sharp maximum or minimum of the potential curve (cf. § 18, especially Fig. 23). Since the area of the surface of the double layer which allows electrons to pass through freely becomes continually smaller as the surface concentration is raised, and the number of places which do not allow the passage of an electron becomes greater, the influence should be the same as of an increased reflection of electrons back into the metal (§ 4), in other words the  $A$  value should fall very much. The sharp increase in the value of  $A$  when the double layer consists of electronegative elements is hereby left quite unexplained.

Schottky\* supposes that the change in the  $A$  value is due to a dependence on temperature of the dipole moments in the double layer. If one assumes that the change of the exponent of  $e$  (this is not equal to the change of the work function, see foot-note † on p. 154) can be represented by a formula

$$\Delta\phi_\theta = C_\theta + \beta_\theta T,$$

\* *Handbuch der Experimentalphysik*, 13, 2, p. 164 (1928).

where  $C$  and  $\beta$  are constants which are only dependent on  $\theta$ , and  $T$  is the absolute temperature, then the emission formula would be

$$i = A_0 T^2 e^{\frac{-\epsilon(\phi_0 + \Delta\phi_\theta)}{kT}} = A_0 T^2 e^{\frac{-\epsilon(\phi_0 + C_\theta + \beta_\theta T)}{kT}}.$$

In this formula  $A_0$  and  $\phi_0$  give the values of  $A$  and of the work function respectively for the pure metal. One may also write

$$i = A_0 e^{\frac{-\epsilon\beta_\theta}{k}} T^2 e^{\frac{-\epsilon(\phi_0 + C_\theta)}{kT}}.$$

If we now set

$$A_\theta = A_0 e^{\frac{-\epsilon\beta_\theta}{k}},$$

we obtain

$$i = A_\theta T^2 e^{\frac{-\epsilon(\phi_0 + C_\theta)}{kT}},$$

in which the numerator of the exponent of  $e$  is again independent of  $T$  and depends only upon  $\theta$ .

According to this view the value and the sign of  $\beta$  determine how much and in which direction  $A$  will change with  $\theta$ . We have seen in § 44 that in the adsorption of barium on nickel\* and of sodium on tungsten† the work function increases with increase of temperature, thus that the emission decreases, at least when  $\theta$  is sufficiently great. In this case then  $C_\theta$  is negative (the work function decreases due to the adsorption)

and  $\beta_\theta$  is positive.  $e^{\frac{-\epsilon\beta_\theta}{k}}$  is thus less than one and  $A_\theta$  is less than  $A_0$ , which is actually observed. However, and this is a great difficulty, even at very small values of  $\theta$ ,  $A_\theta$  is found experimentally to be less than  $A$ , while the dependence on temperature of the dipoles at that point is such that the work function decreases with increasing temperature. Thus at small values of  $\theta$ ,  $\beta_\theta$  is negative, and on the basis of this one should expect an increase in the  $A$  value, which is, however, not found.

The temperature coefficient in the case of double layers with their negative sides away from the surface is unknown, and we are thus unable to judge whether an increase in the value of  $A$  may be interpreted in this case as based on the dependence

\* R. Suhrmann and R. Deponce, *Z. Phys.* **86**, 615 (1933).

† J. H. de Boer and C. F. Veenemans, will appear shortly in *Physica*, **2** (1935).



on temperature of the dipoles, and whether to such a degree as is actually found.

Zwicker\* assumed that the atoms adsorbed on the surface represent rigid dipoles, which are oriented and upon which the thermal movement has a disorienting action. The dependence on temperature is then given by the relation

$$\Delta\phi_\theta = \frac{c_\theta}{T},$$

where  $c$  is a constant dependent only on  $\theta$ , and  $T$  is the absolute temperature.†

If in the actual measurements  $T_0$  represents the average temperature, the expression can be developed into the following series:

$$\Delta\phi_\theta = \frac{c_\theta}{T_0} - \frac{c_\theta}{T_0^2}(T - T_0) = \frac{2c_\theta}{T_0} - \frac{c_\theta}{T_0^2}T.$$

\* C. Zwicker, *Phys. Z.* **30**, 578 (1929).

† According to a private communication from C. Zwicker attention is drawn to the fact that the dependence on temperature of the heat of evaporation of electrons  $L$  (cf. § 2) is given by

$$L = L_0 + \frac{2\epsilon N c_\theta}{T} + \frac{5}{2}RT.$$

In the integrated form (cf. § 2) the expression for  $\log p$  is then

$$\log p = \frac{1}{R} \int \frac{LdT}{T^2} + \text{const.} = -\frac{L_0}{RT} - \frac{\epsilon N c_\theta}{RT^2} + \frac{5}{2} \log T + \text{const.}$$

$$\text{Thus} \quad i = AT^2 e^{\frac{-(L_0 + \epsilon N \frac{c_\theta}{T})}{RT}} = AT^2 e^{\frac{-(\epsilon \phi_\theta + \frac{c_\theta}{T})}{kT}}.$$

The factor 2 in  $\frac{2\epsilon N c_\theta}{T}$  in the expression for  $L$  has disappeared in the integration process.

For the same reason the dependence on temperature of  $\phi$ ,

$$\Delta\phi_\theta = C_\theta + \beta_\theta T,$$

in the treatment of Schottky (see above) does not mean that the dependence of  $L$  on temperature is also in this form.

If  $L$  could be written as

$$L = L_0 + \beta_\theta T + \frac{5}{2}RT,$$

the emission equation would be

$$i = AT^2 e^{-\frac{\epsilon \phi_0}{kT} - \frac{\beta_\theta}{T}} \times T^{\frac{5}{2}}.$$

The expression for the electron emission then becomes

$$i = A_0 T^2 e^{\frac{-\epsilon \left( \phi_0 + \frac{2c_\theta}{T_0} - \frac{c_\theta}{T_0^2} T \right)}{kT}},$$

or

$$i = A_0 e^{\frac{\epsilon c_\theta}{kT_0^2}} T^2 e^{\frac{-\epsilon \left( \phi_0 + \frac{2c_\theta}{T_0} \right)}{kT}},$$

so that

$$A_\theta = A_0 e^{\frac{\epsilon c_\theta}{kT_0^2}}.$$

Double layers which lower the work function ( $c_\theta$  negative) have thus according to this conception a lower  $A$  value; double layers which raise the work function ( $c_\theta$  positive) a higher  $A$  value than pure metals. This is in agreement with what is always observed experimentally. The assumption, however, of rigid dipoles which lead to this result is not in the least in agreement with the facts,\* in any event not in those cases where sodium or barium are adsorbed on metals. Perhaps the conception can be applied to oxide films and similar surface coverings.

It must be noted that Richardson† pointed out that when the electron emission of a metal is changed by an alteration in its covering of gas, the  $A$  value and the work function always vary in such a way that there is a linear relation between  $\log A$  and  $\phi$ :

$$\phi_\theta = a \log A_\theta + b,$$

where  $a$  and  $b$  represent constants.

This relation may be deduced from the conception of Zwikker as well as from that of Schottky. According to Zwikker

$$\ln A_\theta = \ln A_0 + \frac{\epsilon c_\theta}{kT_0^2},$$

and

$$\phi_\theta = \phi_0 + \frac{2c_\theta}{T_0},$$

and therefore

$$\phi_\theta = \frac{2k}{\epsilon} T_0 \ln \frac{A_\theta}{A} + \phi_0.$$

\* Cf. R. Suhrmann and R. Deponce, *Z. Phys.* **86**, 633 (1933).

† O. W. Richardson, *Proc. roy. Soc. A*, **91**, 524 (1915); cf. also K. H. Kingdon, *Phys. Rev.* **24**, 510 (1924); S. Dushman and J. W. Ewald, *Phys. Rev.* **29**, 87 (1927); C. Zwikker, *Phys. Z.* **30**, 578 (1929); L. A. DuBridge, *Proc. Nat. Acad. Sci.*, Wash., **14**, 788 (1928); S. Dushman, *Rev. Mod. Phys.* **2**, 381 (1930).

According to Schottky's representation the relation between  $\log A_\theta$  and  $\phi_\theta$  can be deduced by assuming in addition that  $\Delta\phi_\theta$  is proportional to  $\theta$ ;  $C_\theta$  and  $\beta_\theta$  are then proportional to  $\theta$ , and  $\log A_\theta$  and  $\phi_\theta$  both change linearly with  $\theta$ . There is, however, not a single case where  $\Delta\phi_\theta$  is proportional to  $\theta$  over the whole adsorption range.

### § 50. Caesium on an oxygen-covered tungsten surface and similar cases.

Caesium is more strongly adsorbed on a tungsten surface which is partially covered with oxygen than on a clean tungsten surface. The electron emission of these complex surfaces, which are usually indicated in the literature by the symbol W-O-Cs cathodes, is quite analogous to the emission of W-Cs cathodes, which were treated in Chap. III.\* Here again it has been especially the work of Langmuir and his coworkers† and of Becker‡ which has shown us the essential characteristics of this adsorption. Although the adsorption of oxygen lowers the electron emission of tungsten very much, the adsorption of caesium on these surfaces gives such an increase in the emission again that it may become  $10^6$  times as great as that of a [W]-Cs surface. This is another case of the establishment of a dynamic equilibrium between the layer adsorbed on the tungsten surface and the caesium atoms in the surrounding vapour. The adsorption equilibrium is thus here also dependent both on the filament temperature and on the vapour pressure of the caesium, that is to say on the temperature of the walls of the tube when saturated caesium vapour is used.

When oxygen is allowed to be adsorbed on a clean, cold tungsten filament, and thereafter, also at an ordinary temperature, caesium is allowed to be adsorbed, a surface is obtained which is not yet capable of high electron emission. The surface must first be activated. Even when the clean filament is first heated at about  $1900^\circ\text{K}$ . in oxygen at a pressure of

\* We shall indicate these cathodes by the symbols [W]-O-Cs and [W]-Cs cathodes. The metal in the brackets is the base metal on which ions or atoms, with or without intermediate layers, are adsorbed.

† I. Langmuir and K. H. Kingdon, *Proc. roy. Soc. A*, **107**, 61 (1925).

‡ J. A. Becker, *Phys. Rev.* **28**, 341 (1926).

about 0.02 mm. for a few seconds, after which, the filament being cooled and the oxygen pumped away, caesium is admitted, a surface with a high emission is not obtained. At temperatures between 700 and 1000° K. the electron emission is still quite small. In order to obtain a good emission the filament must now be heated for several seconds at, for instance, 1600° K.\* After this last heating the filament is in an active state, and one obtains at a filament temperature of 1000° K. an electron emission of 0.35 amp./cm.<sup>2</sup> if the vapour pressure of the caesium is controlled by a tube temperature of 30° C. During the activation part of the oxygen will probably evaporate, whereupon the remaining oxygen ions and the caesium ions and atoms will take up their most favourable positions. The caesium ions are here bound not only by the tungsten surface (image force) but also by the negative oxygen

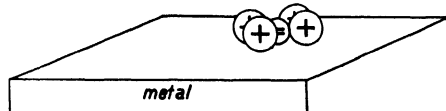


Fig. 61. Diagram representing the adsorption of  $\text{Cs}^+$  ions next to  $\text{O}^{--}$  ions on a tungsten surface.

ions, and are thus bound much more tightly to the surface than by their adsorption on pure tungsten only. We must hereby not imagine, as is often done, that the tungsten surface is first covered by a monatomic layer of oxygen, upon which a monatomic layer of caesium is then adsorbed. The case is quite different, and we find caesium ions adsorbed on the tungsten surface next to oxygen ions (Fig. 61). The concentration of oxygen and caesium on the surface is not known. Under the most favourable conditions according to research by Langmuir and Villars† the oxygen ions will only cover a small portion of the surface, while around each oxygen ion more than one caesium ion, probably three to seven, will group themselves. We may further expect that caesium atoms will add themselves next to the caesium ions and help to lower the work function by means of their dipoles (cf. § 28). Since relatively

\* K. H. Kingdon, *Phys. Rev.* **24**, 510 (1924).

† I. Langmuir and D. S. Villars, *J. Amer. chem. Soc.* **53**, 486 (1931).

many caesium ions find places about each oxygen ion, the raising of the work function which was caused by the adsorption of oxygen is easily compensated for by the positive caesium ions. The stronger bond of the caesium ions next to the oxygen ions has still this other result, that even after this compensation more caesium ions can be adsorbed than on pure tungsten before the point is reached when the adsorption of caesium atoms takes place more easily than that of ions. Thus the work function is finally lowered to a greater extent than in the adsorption of caesium on pure tungsten. According to the measurements of Kingdon, under the most favourable circumstances the values of  $A$  and  $\phi$  in the emission formula are the following:

$$A = 0.001 \text{ amp./deg.}^2 \text{ cm.}^2, \quad \phi = 0.71 \text{ volt.}$$

To what extent the work function is lowered by the adsorption of caesium in this case cannot be measured, since we do not know what the work function is of the tungsten filament covered with just that amount of oxygen which is present on the final [W]-O,Cs cathode.

Because the work function is lower, but more especially because the caesium ions are more tightly bound, higher values of the electron emission can be attained than with [W]-Cs cathodes, since in this case the cathode can be heated to a higher temperature without the danger that the emission will fall again because of the evaporation of too much caesium (see Fig. 62). According to the investigations of Becker\* the amount of adsorbed caesium under optimum conditions is about 10 per cent. greater than that on [W]-Cs cathodes under corresponding conditions.

Langmuir and Villars,† starting with optimum conditions, obtained surfaces with properties which lay between those of the [W]-O,Cs and the [W]-Cs cathodes, by evaporating a portion of the oxygen at a high temperature. In this way they studied the properties of the evaporation of oxygen adsorbed on tungsten (§ 46).

\* J. A. Becker, *Phys. Rev.* **23**, 341 (1926).

† I. Langmuir and D. S. Villars, *J. Amer. chem. Soc.* **53**, 486 (1931).

Complex cathodes which are probably analogous to the above-mentioned [W]-O,Cs cathode in make-up have also been studied in photoelectric work. With practically all photoelectric cathodes which are built up of an alkali metal and an electronegative component together on a metal a spectrally selective photoeffect is found, which indicates that at least part of the emitted electrons do not originate in the supporting metal, but in the adsorbed atoms themselves (see Chap. v, § 43, and Chap. ix). In many cases the emission at the photoelectric threshold may even be ascribed to the freeing of electrons from

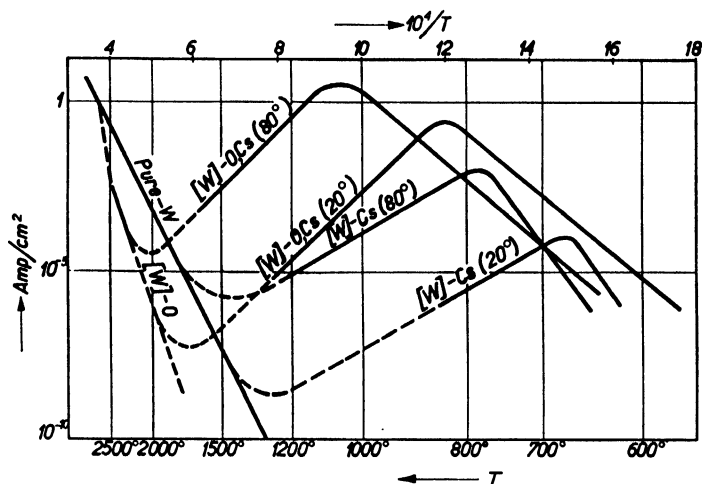


Fig. 62. Electron emission as a function of temperature for [W]-O,Cs and [W]-Cs cathodes at Cs vapour pressures corresponding to a bulb temperature of 20 and 80  $^{\circ}\text{C}$ . Figure taken from I. Langmuir, *Industr. Engng Chem.* **22**, 390 (1930).

the adsorbed atoms, and in most cases we do not know whether under certain conditions an electron emission from the underlying layer takes place, which is modified by an electrical double layer. In a detailed investigation Koller\* mentions two kinds of cathodes which may be indicated by the symbols [Ag]-O,Cs and [Ag]-Cs<sub>2</sub>O-Cs. The first of these cathodes, the [Ag]-O,Cs cathode, is according to its properties and its method of preparation most nearly like the [W]-O,Cs cathode. It is made by heating a clean silver surface in oxygen, cooling it, pumping off the excess oxygen, admitting caesium, and then

\* L. R. Koller, *Phys. Rev.* **36**, 1639 (1930).

heating it again in order to activate the cathode. The whole procedure is thus the same as for the preparation of [W]-O,Cs cathodes; only the temperatures are of course different in this case. The first heating takes place at 360° C., the second in the presence of caesium at 300° C. In contrast with the [Ag]-Cs<sub>2</sub>O-Cs cathodes, which will be treated in detail later (§ 68), the [Ag]-O,Cs cathode has no selective maximum in the visible spectral range, but the photoemission increases regularly from the photoelectric threshold at about 8000 Å. until a maximum is reached in the ultraviolet at about 3500 Å. The spectral sensitivity is thus quite analogous to that found in the adsorption of alkali metals on clean metal surfaces (Chap. v), and thus the structure of the [Ag]-O,Cs cathode may be considered to be similar to that of the [W]-O,Cs cathode, viz. caesium ions adsorbed next to the oxygen ions on the metal surface, and afterwards also caesium atoms (see also § 68).

[W]-O,Ba cathodes were investigated by J. W. Ryde and N. L. Harris.\* The emission can be represented by

$$i = 0.5 T^2 e^{-\frac{16.750}{T}} \text{ amp./cm.}^2,$$

thus  $\phi_0 = 1.44$  volts. In § 32 we saw that the same investigators found for the [W]-Ba cathodes  $\phi_0 = 1.56$  volts. Ryde and Harris also mention cases in which oxygen is admitted to a [W]-Ba cathode and where  $\phi_0$  then rises to 1.9 volts. They suppose in this case that the oxygen is situated on the barium. This cathode is unstable compared to the [W]-O,Ba cathode and easily passes over into the form of the [W]-O,Ba cathode.

### § 51. Other cases of complex adsorbed layers.

In photoelectric literature examples are mentioned where the adsorption of water vapour increases the photoelectric sensitivity. *A priori* one would not expect this, since because of the asymmetric position of the dipole in the water molecule whereby the hydrogen ions are nearer the outside, one would be inclined to assume that the positive side of the water

\* Mentioned by E. K. Rideal, *An Introduction to Surface Chemistry*, p. 224, Cambridge (1930). A survey of the experiments of Ryde and Harris may also be found in the recently published book by A. L. Reimann, *Thermionic Emission*, pp. 159-77 (1934).

dipole is directed toward the metal and the negative side away from the metal. It is of course possible that thanks to the van der Waals attractive forces (§ 13) the oxygen side is toward the metal, so that the dipole has its positive end directed away from the surface. In many experiments, however, the water has not been adsorbed on a clean metal surface, but as in Klumb's\* experiments on a metal surface which was so far outgassed that the photoelectric threshold lay much farther toward the long wave-lengths than that of the pure metal. These surfaces probably contain adsorbed positive hydrogen ions. If water molecules are added to such a surface one may imagine that due to the attraction of the positive hydrogen ions the water dipoles are directed with their positive ends away from the surface. This would explain Klumb's result that the adsorption of water vapour gives an increase of photoelectric current.

Similar results were obtained by Abendroth.† He allowed water, pyridine, propionic acid and benzene to be adsorbed on platinum which was not completely outgassed, and observed in all cases an increase in the photoelectric sensitivity. Only upon the adsorption of larger amounts was the sensitivity again lowered. One might imagine that the positive hydrogen ions direct the dipoles of the adsorbed material in such a way that the work function is still further lowered, while the molecules without permanent dipoles (benzene) are polarized in the same direction. The decrease of the work function by the polarized benzene molecules is then quite analogous to that by the polarized caesium atoms adsorbed next to caesium ions.

**§ 52. The influence on the work function due to thorium and platinum and the absence of such influence due to cadmium and mercury.**

Before leaving the subject of the changes in the work function brought about by adsorbed films and passing on in the second part of this book to the treatment of the emission of electrons from adsorbed atoms and molecules, a few typical examples must be mentioned.

\* H. Klumb, *Z. Phys.* **47**, 652 (1928).

† B. Abendroth, *Z. Phys.* **85**, 530 (1933).



The metals which decrease the work function in thermionic emission (alkali metals, alkaline earth metals, thorium, etc.) have a similar influence in photoelectric emission. The case of the alkali metals has already been discussed in detail. Thorium on tungsten was investigated by Linford\* who found the photoelectric threshold at  $4900 \text{ \AA}$ . corresponding to a work function of 2.52 volts, a value in quite good agreement with the work function determined from the thermionic emission (§ 38). As was true in the case of the thermionic emission the work function is here also higher for pure thorium, and the photoelectric threshold is at shorter wave-lengths than for a surface covered with adsorbed thorium.†

In § 37 we have seen that in accelerating fields the change of the work function in the case of adsorbed layers is much greater than is given by the Schottky relation. Linford also finds in the case of adsorbed thorium a shift of the photoelectric threshold to  $5500 \text{ \AA}$ . when he increases the field to 48,200 volts/cm.; Schottky's relation would have given a shift only to  $5100 \text{ \AA}$ .

The adsorption of metals does not always produce a lowering of the work function. According to Sears and Becker‡ the condensation of platinum on tungsten causes a decrease of the electron emission. The electron emission is especially strongly lowered by the addition of the first adsorbed layer of platinum, after which the decrease continues slowly when more platinum is condensed until the value for pure platinum is reached.

If metals are not adsorbed when they are condensed on surfaces, but agglomerate, they have no influence on the work function.§ Thus cadmium and mercury are not adsorbed on many surfaces (as, for example, on metal surfaces which are covered with oxygen, § 45), but form clusters which upon being examined photoelectrically exhibit the properties of cadmium or mercury in bulk.

\* L. B. Linford, *Phys. Rev.* **36**, 1100 (1930).

† H. C. Rentschler, D. E. Henry and K. O. Smith, *Phys. Rev.* **40**, 1045 (1932).

‡ R. W. Sears and J. A. Becker, *Phys. Rev.* **43**, 1058 (1933).

§ D. Roller, W. H. Jordan and C. S. Woodward, *Phys. Rev.* **38**, 395 (1931); D. Roller and D. Wooldridge, *Phys. Rev.* **45**, 119 (1934).

## CHAPTER VII

### THE ABSORPTION OF LIGHT BY MATTER IN THE GASEOUS STATE

#### § 53. Potential curves and vibration levels.

In § 12 we became acquainted with the use of potential curves in the treatment of chemical combination (see Fig. 11), and we used these potential curves repeatedly in Chap. II and later chapters. The question now before us is what happens when energy is added to a molecule. If this energy is added in the form of heat, thus thermal energy, the atoms in the mole-

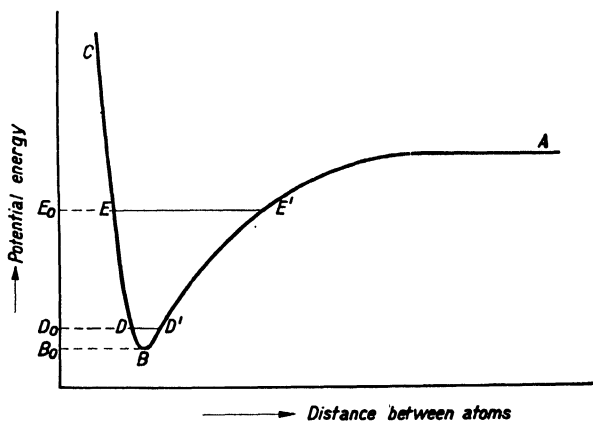


Fig. 63. Potential curve, showing some vibration levels.

cule begin to vibrate with respect to each other. As a matter of fact the atoms also vibrate with respect to each other even at absolute zero (zero point vibration), so that the molecule is never exactly at the minimum  $B$  of the potential curve (Fig. 63). The zero point vibration is, however, such that the atoms take up distances from each other through their reciprocal motion which lie between the values  $D_0D$  and  $D_0D'$ ; the most common distance is, however,  $B_0B$ . The zero point vibration is thus represented by that part of the potential curve which is indicated by the letters  $DBD'$ . The difference between  $D$  or  $D'$  and  $B$ , i.e.  $D_0B_0$ , is the zero point energy.

If thermal energy is now given to the molecule, for example

an amount which can be represented by the difference in height  $D_0E_0$  in Fig. 63, then the atoms execute vibrations which are represented by  $EBE'$  on the potential curve. If the separation of the atoms during these vibrations is given by  $E_0E$ , then all the energy taken up is present in the form of potential energy; after half a vibration the separation has become  $E_0E'$  and the energy is again in the form of potential energy. During the vibration the energy of the vibrating atoms goes through a continual change from potential to

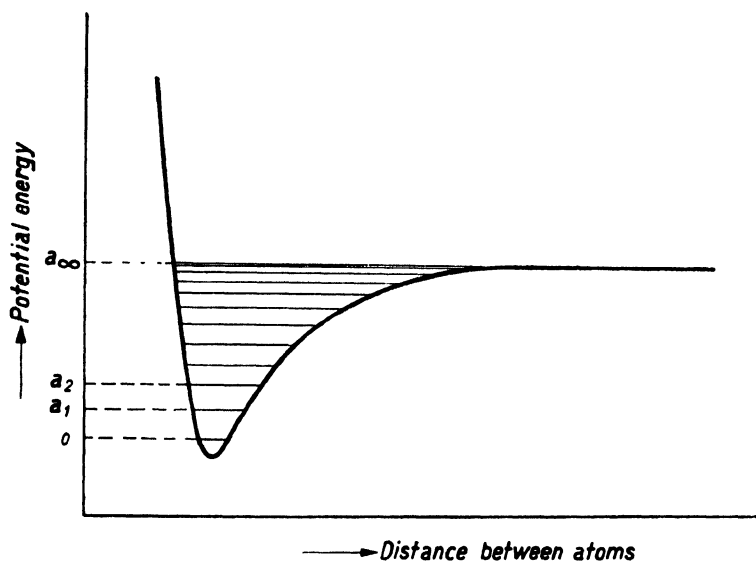


Fig. 64. Potential curve with a converging series of vibration levels.

kinetic and *vice versa*. At the moment when the separation is  $B_0B$  all the energy is present in the form of kinetic energy. At separations greater than  $B_0B$  the atoms attract each other, at separations less than  $B_0B$  they repel each other.

We have seen in § 11 that an electron can exist only in certain states of energy with respect to the remainder of the atom. As a consequence the atom cannot take up any arbitrary quantity of energy, but only very definite quantities which represent the difference of energy between one of the permitted excited states and the normal state. We now meet a similar rule for the assumption of vibration energy by molecules: the molecule cannot take up any arbitrary amount of vibration energy, but

states in which a molecule can exist, and which are represented in Fig. 64 by horizontal lines. The molecule can take up only the amounts of energy

$$oa_1, oa_2, oa_3, \dots, oa_\infty.$$

These quantities of energy form a converging series, since the differences become steadily less. When the quantity  $oa_\infty$  is taken up, then after half a vibration the horizontal part of the potential curve is reached, which means that the atoms fly apart and that the molecule is thus dissociated. A quantity of energy just equal to the dissociation energy has been given to the molecule (cf. the analogous case of the converging series of the excited states of the atom in § 11). Above  $oa_\infty$  any amount of energy can be given to the molecule; the atoms then fly apart with kinetic energy equal to the amount taken up in excess of  $oa_\infty$ .

#### § 54. The Franck-Condon principle.

By means of research on the subject of potential curves Franck\* derived a principle which is very important for the explanation of band spectra. Let us imagine two atoms  $X$  and  $Y$  which can form a molecule  $XY$ , and further that one of these atoms,  $X$  for example, may exist in an excited state  $X'$ , and that in this excited state it is also able to form a chemical compound with  $Y$ . Then we may draw the potential curves of the molecules  $XY$  and  $X'Y$  with respect to the same axes (Fig. 65) if the level  $X' + Y$  is made higher than  $X + Y$  by an amount  $Q_e$  which represents the excitation energy of the atom  $X$  (cf. also the potential curves in § 13, Figs. 12 and 13). In an existing chemical compound  $X$  can also be transformed into its excited state  $X'$ , which is represented by the passing from a point on the lower potential curve to a point on the higher curve. According to the principle originated by Franck and worked out more quantitatively by Condon† (the Franck-Condon principle), this transition from one curve to the higher one has the

\* J. Franck, *Trans. Faraday Soc.* **21**, 536 (1925); *Z. phys. Chem.* **120**, 144 (1926). Cf., in addition, H. Sponer, *Z. Elektrochem.* **34**, 483 (1928); *Ergebn. exakt. Naturw.* **6**, 75 (1927); *Leipziger Vorträge*, p. 107 (1931); J. Franck, *Z. Elektrochem.* **36**, 581 (1930).

† E. U. Condon, *Phys. Rev.* **28**, 1182 (1926); **32**, 858 (1928).

greatest probability when the distance between the atoms is thereby unchanged. For a molecule in its normal state ( $DD'$ ) this means that the transition takes place mainly in the shaded portion of Fig. 65, thus toward the portion of the upper curve lying between  $I$  and  $H$ . If the transition takes place due to the absorption of light (other causes are also possible, for example, electronic collision; we are, however, interested mainly in the transition caused by the absorption of light), then quantities of energy are taken up in the absorption which lie between

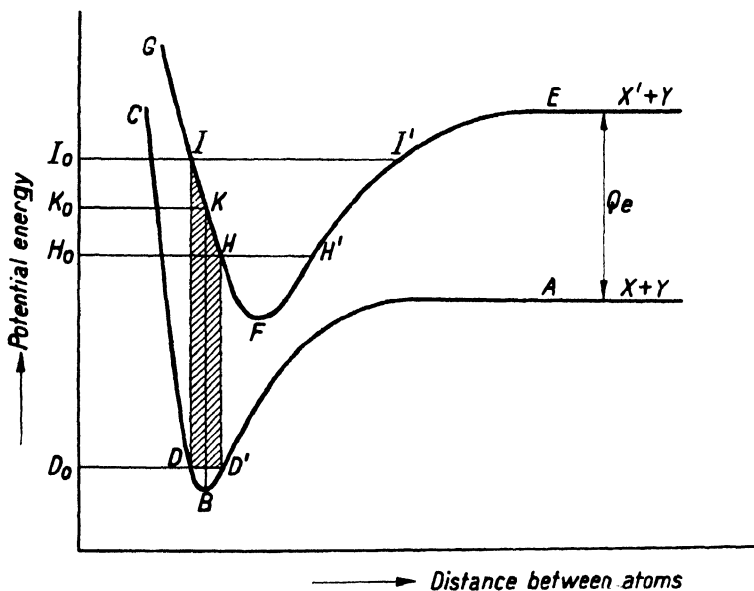


Fig. 65. Potential curves for two molecules  $XY$  and  $X'Y$ , showing the energy changes, according to the Franck-Condon principle.

$D_0H_0$  and  $D_0I_0$ . The excited molecule  $X'Y$  is then not in *its own normal state*, but in an *excited state* with respect to vibration energy also, which vibration state lies between  $HH'$  and  $II'$ . Instead of a single transition as with an atom ( $X$  to  $X'$ ) we here have the transition from one definite level to a large number of excited levels, which all vary in vibration energy. Since, in addition, for every vibration state there is a large number of rotation states (rotations of the atoms about their common centre of gravity), for every transition from

$DD'$  to one of the vibration levels between  $HH'$  and  $II'$  there is an absorption band made up of fine lines, and the whole process of absorption gives rise to a system of bands. Thus while in single atoms an electron jump gives only a single absorption line, with molecules we get a complete band system, with each band made up of fine lines.\* The maximum of the light absorption is given by the passage from  $B$  to  $K$ , to which the energy  $D_0K_0$  corresponds. (At  $B$  the molecule also possesses the zero point energy so that the energy level—potential + kinetic energy—is given by  $DD'$ .)

Since the zero point energy is only a small quantity (several tenths of a volt) we shall from now on start from the point  $B$  when considering transitions from the normal state, keeping in mind that absorption is also observed to the right and to the left of the place which represents the maximum absorption in the absorption spectrum, since transitions also take place which start at points lying to the right and to the left of  $B$  and end even at points to the left of  $I$  and to the right of  $H$ , since the shaded region represents only the places where there is the greatest probability of transition.

### § 55. Dissociation caused by the absorption of light.

When the probability of transition due to the absorption of light is such that in the transition from the normal state  $B$  a point  $H$  is reached (Fig. 66) which lies above the level  $GD$ , then the excited molecule will fall apart during the first half-vibration which follows the elementary process of light absorption. Following the absorption of light and as a result of it, a dissociation of the molecule has taken place. In the absorption spectrum such an event is manifested by the presence of regions of continuous absorption. As we have seen in § 54 the transition to the vibration levels of the excited molecule gives rise to absorption bands which are made up of exceedingly fine lines. In contradistinction to this discrete band

\* A single molecule can of course undergo only one of the many possible transitions to an excited level. In all experiments we are dealing with a great number of molecules, so that all possible transitions take place, and the complete absorption band is formed.

structure is the region of continuous absorption which results from a transition to a point on the potential curve lying above  $GD$ . This can be understood by comparison with § 53, where we have seen that in that region all energies are possible. Here the atoms upon dissociation fly apart with kinetic energy which may assume any arbitrary amount and is not governed by quantum rules. Thus we obtain an absorption spectrum which at its long-wave end is made up of a number of discrete bands which converge to a definite limit in the direction of shorter wave-lengths, whereupon a region of continuous absorption

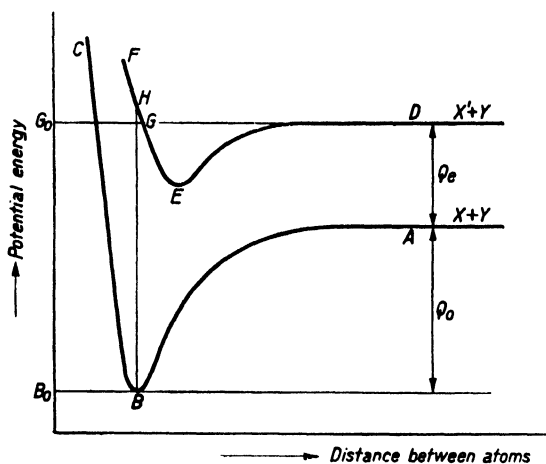


Fig. 66. Dissociation into  $X' + Y$  by absorption of light.

follows directly at shorter wave-lengths (cf. §§ 11 and 56 for the analogous process with atoms).

In this optical dissociation the molecule does not in general dissociate into the same components as would result from heating. In the case represented in Fig. 66 thermal dissociation would result in the normal atoms  $X$  and  $Y$ , while the optical dissociation gives rise to the excited atom  $X'$  and the normal atom  $Y$ .

The limit of convergence can be very accurately determined in many cases, and can be immediately deduced from Fig. 66, where it is given by the sum of the dissociation energy into normal atoms ( $Q_0$ ) and the energy of excitation ( $Q_e$ ),

$$h\nu_c = Q_0 + Q_e,$$

$h$  being Planck's constant (§ 2) and  $\nu_c$  the frequency of the limit of convergence. Since  $Q_c$  is known with a high degree of accuracy in most cases the value of the dissociation energy into normal atoms can be calculated with the same accuracy from the value of  $h\nu_c$ .

We shall mention briefly several examples. Iodine vapour gives an absorption spectrum which consists of discrete bands, converging to the limit  $4995\text{ \AA.}$ ; directly following this convergence limit toward shorter wave-lengths is a band of continuous absorption. By radiation within this continuous absorption band an iodine molecule is split into a normal iodine atom and a metastable iodine atom whose excitation energy is  $0.937$  electron volt.\* The energy corresponding to the convergence limit is  $2.469$  electron volts, so that for  $Q_0$ , the work done in splitting the iodine molecule into two normal atoms,  $1.532$  electron volts is found. This value obtained optically agrees very well with the well-known energy of dissociation,  $1.50$  electron volts ( $34.5$  kg. cal./mol.) found chemically. That a dissociation into atoms is obtained by the absorption of light has been proved experimentally by various investigators.†

Division into one normal and one excited atom has been found in the cases of molecules of the other halogens and of compounds of the halogens with each other, while it also occurs with compounds such as the silver halides and thallium halides in vapour form. As we have seen in § 13 the molecules of these compounds in the vapour state are built up of atoms. The ionic molecule must be considered to be in an excited state; there are, however, other excited states of the molecule possible in which either the metal atom or the halogen atom exists in the excited state. These latter states can be reached by the taking up of a smaller quantity of energy than is required for transition to the potential curve of the ionic molecule. The absorption band of the silver halides which lies at the longest wave-

\* L. A. Turner, *Phys. Rev.* **27**, 397 (1926).

† E. G. Dymond, *Z. Phys.* **34**, 553 (1925); K. F. Bonhoeffer and L. Farkas, *Z. phys. Chem.* **132**, 235 (1928); L. A. Turner, *Phys. Rev.* **31**, 983 (1928); H. Senftleben and E. Germer, *Ann. Phys., Lpz.*, **2**, 847 (1929); L. A. Turner and E. W. Samson, *Phys. Rev.* **37**, 1023 (1931).



lengths (for AgI at about  $3500\text{ \AA}$ .) corresponds to a division of the molecule into a normal silver atom and a metastable halogen atom.\* Toward the ultraviolet follow bands which correspond to a division into a normal halogen atom and an excited silver atom. In the case of the thallium halides, beginning at the long-wave end of the spectrum, one finds first the band which corresponds to the division into a normal thallium atom and an excited halogen atom, and then following bands corresponding to a division into normal halogen and excited thallium.† Thereupon in the case of TII an absorption band

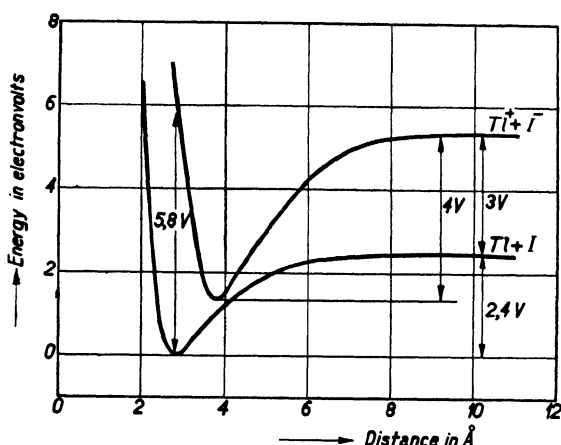


Fig. 67. Potential curves for the ionic and atomic molecules TII.  
A. Terenin and B. Popov, *Phys. Z. Sowjet.* 2, 315 (1932).

follows at still shorter wave-lengths (at about  $2130\text{ \AA}$ ., i.e.  $5.8$  electron volts), which indicates the division of the molecule into a thallium ion and an iodine ion,‡ as is indicated schematically in Fig. 67.

The molecules of the alkali halides in the vapour state also consist of ions; the potential curve of the atomic compound is in this case an excited state for the ionic molecule (§ 13). As is schematically indicated in Fig. 68 light absorption (transition from  $E$  to  $G$ ) leads in this case to a division into two *normal*

\* J. Franck and H. Kuhn, *Z. Phys.* 43, 164 (1927); 44, 607 (1927).

† K. Butkow, *Z. Phys.* 58, 232 (1929).

‡ A. Terenin, *Phys. Z. Sowjet.* 2, 377 (1932).

atoms.\* Upon the absorption of light an electron jumps from the halogen ion to the metal ion, so that both ions pass over into the atomic form and the molecule falls apart. This electron jump also takes place in the absorption of light by substances in the solid state, for example, with the alkali halides as well as with the silver and thallium halides, which, as we have noted in § 13, in the solid state are built up of ions. We shall return later (§§ 73 and 87) to the subject of the absorption of light by matter in the solid state.

Following the first absorption band in the case of the alkali halides, to which band a division into two normal atoms cor-

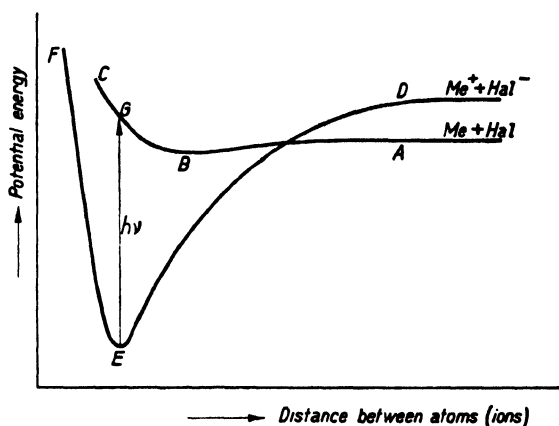


Fig. 68. Dissociation of an ionic molecule of alkali halide into two normal atoms by absorption of light.

responds, there come various bands lying at shorter wavelengths. The absorption of light within these bands causes the formation of one normal and one excited atom.

### § 56. Photoionization of caesium vapour.

We have seen in § 11 that an atom can be ionized by radiation by light of sufficiently short wave-length. The atom must thereby take up a quantity of energy which is equal to the ionization energy. The  $h\nu$  value of the limit of convergence of the lines of the absorption spectrum represents exactly this energy. Light of a shorter wave-length than that correspond-

\* Cf. J. Franck, H. Kuhn and G. Rollefson, *Z. Phys.* **43**, 155 (1927); K. Sommermeyer, *Z. Phys.* **56**, 548 (1929).

ing to the ionization limit may also be absorbed by the atom, and may also give rise to ionization. The excess of energy in the absorbed light quantum above the ionization energy is then recovered as kinetic energy of the electron which is split off, and of the remaining atom. Thus also in the absorption spectrum of an atom after the series of discrete absorption *lines* which converges in the direction of shorter wave-lengths, there follows at still shorter wave-lengths a region of continuous absorption just as in the molecular absorption spectrum a band of continuous absorption follows the converging series of discrete bands. These absorption regions are continuous because the remaining kinetic energy is *not* bound by quantum rules, and may therefore assume any arbitrary value.

In the case of caesium the limit of convergence of the line spectrum lies at  $3184\text{ \AA}$ . (ionization potential  $3.88$  volts,



Fig. 69. Absorption spectrum of caesium.

see § 11); the region of continuous absorption begins at this point and is here also maximum in intensity. The intensity decreases toward shorter wave-lengths (Fig. 69). We may assume that the absorption of light in the region of continuous absorption is entirely due to the photoionization, so that the photoionization curves are identical with the absorption curves. As a matter of fact the photoelectric current obtained by the irradiation of caesium vapour with light of various wave-lengths is at a maximum at  $3184\text{ \AA}$ . and decreases for shorter wave-lengths. According to Lawrence and Edlefsen\* the photoionization decreases steadily with decreasing wave-length; other investigators, however, found a minimum after which the photoionization rose again. Little,† for example, found a minimum at  $2800\text{ \AA}$ .; Mohler, Foote and Chenault,‡ using

\* E. O. Lawrence and N. E. Edlefsen, *Phys. Rev.* **34**, 233 (1929).

† E. M. Little, *Phys. Rev.* **30**, 109, 963 (1927).

‡ F. L. Mohler, P. D. Foote and R. L. Chenault, *Phys. Rev.* **27**, 37 (1926).

caesium vapour at  $182^{\circ}\text{C}$ ., found a minimum at about  $2700\text{\AA}$ .; Cooke\* mentions a minimum at  $2800\text{\AA}$ . The more recent measurements by Kunz† of the ionization of caesium vapour and by Braddick and Ditchburn‡ of its light absorption give a minimum at about  $2800\text{\AA}$ . In the case of potassium also the results of Lawrence and Edlefsen do not agree with those obtained by Mohler and his collaborators.§

One might expect that irradiation by light of wave-length greater than  $3184\text{\AA}$ . would produce no photoionization. This is, however, not so. With caesium as well as with rubidium and potassium one observes ionization at wave-lengths greater than the ionization limit. A direct photoionization of the atom cannot take place in this case, since the energy of the radiated quantum is not sufficient. It appears that ionization may be observed especially by irradiation with wave-lengths which correspond to the absorption lines, but that irradiation with wave-lengths which lie between the absorption lines of caesium vapour also leads to the giving up of electrons. Very careful research by Mohler and Boeckner|| and by Freudenberg¶ has proved that the giving up of electrons due to irradiation by light corresponding to the absorption lines is the result of a secondary process. In agreement with a view first presented by Franck\*\* in 1928 one must assume that an excited atom collides with a normal one and gives rise to a molecular ion  $\text{Cs}_2^+$  and one electron. Not all the lines of the absorption spectrum can be connected with this process; the energy of the red absorption line at  $8521\text{\AA}$ . cannot by itself give rise to this process, and at the blue absorption line at  $4555\text{\AA}$ . there must be an additional quantity of energy supplied. We shall

\* F. W. Cooke, *Phys. Rev.* **38**, 1351 (1931).

† J. Kunz, *Phil. Mag.* (7), **17**, 483 (1934).

‡ H. J. J. Braddick and R. W. Ditchburn, *Nature*, Lond., **131**, 133 (1933).

§ Cf. A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, pp. 251–8 (1932).

|| F. L. Mohler and C. Boeckner, *Bur. Stand. J. Res.*, Wash., **5**, 51 (1930).

¶ K. Freudenberg, *Z. Phys.* **67**, 417 (1931).

\*\* J. Franck, cited in B. Gudden, *Lichtelektrische Erscheinungen*, p. 226 (1928).

attempt to explain the observed phenomena in connection with the potential curves drawn in Fig. 70. Two caesium atoms can combine to form a caesium molecule ( $\text{Cs}_2$ ), whereby the combining energy is about 0.35 electron volt (curve *abc*). When irradiated with light of  $3184 \text{ \AA}$ . or shorter, a caesium atom can be transformed into a caesium ion ( $\text{Cs}^+$ ) and one electron. This caesium ion can form a molecular ion  $\text{Cs}_2^+$  by collision with a caesium atom (curve *def* and the shaded portion above it). If light of a wave-length of  $3876 \text{ \AA}$ . is used an excited caesium

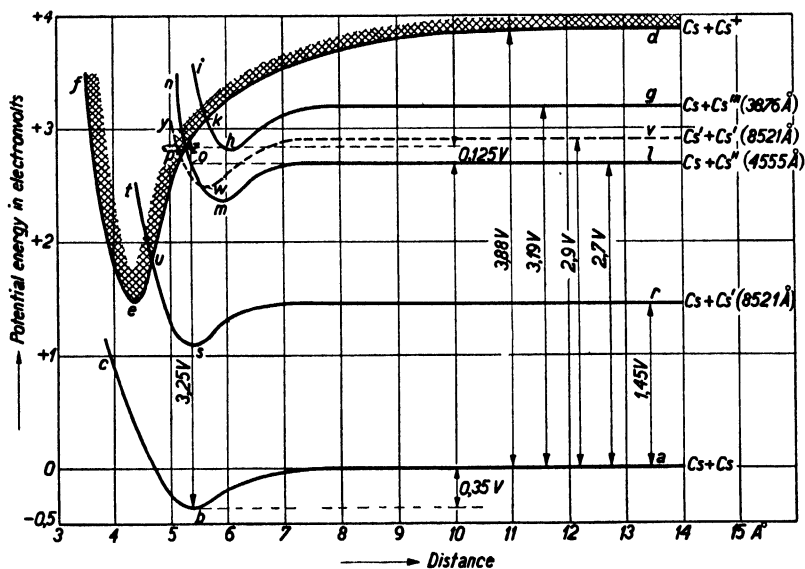


Fig. 70. Potential curves, referring to the different ionization processes in Cs vapour.

atom results which we shall indicate by the symbol  $\text{Cs}'''$ , and which has absorbed 3.19 electron volts. If this  $\text{Cs}'''$  collides with a normal caesium atom before it has lost its extra energy by radiation it can also form a molecule (curve *ghi*). In the formation of such a molecule, however, the combining energy which is freed cannot be dissipated unless there is another body (a third atom or molecule or the wall of the tube) which can take up the energy. If there is no such possibility of dissipating the liberated energy then the atoms continue to vibrate with respect to each other. The molecule may in this case, unless there are special circumstances, immediately fall apart

again; the  $\text{Cs}_2^+$  molecule as it is formed in the vapour from  $\text{Cs}^+$  and  $\text{Cs}$  will probably also immediately dissociate. The potential curve  $ghi$ , however, lies in such a position that its intersection  $k$  with the curve  $def$  is lower than the level  $g$ . This means that in the collision of  $\text{Cs}'''$  and  $\text{Cs}$  this point is reached, or in other words that the atoms are at such a distance from each other and possess such a reciprocal potential energy as is given by the coordinates of point  $k$ . Point  $k$  happens also to be a point on the curve  $def$ , or, in other words, at the same distance apart and with the same energy content the system  $\text{Cs}^+$ ,  $\text{Cs}$  + a free electron, is also possible. In such a case there is always a certain probability that one system will actually pass over into another. In this particular case it leads to ionization: from the system  $\text{Cs}'''$ ,  $\text{Cs}$  results a molecular ion  $\text{Cs}_2^+$  and an electron which is no longer bound. The study of the so-called predissociation spectra has, to be sure, shown that there is a great probability of such a transition only when there is practically no extra kinetic energy present at the intersection (in other words, when the vibrating atoms do not move rapidly over this point, but arrive there just at the turning point of a vibration). In this particular case, however, all points on the part of the curve  $ki$  give a probability of transition, since they fall in the shaded portion. The electron and the resulting  $\text{Cs}_2^+$  ion will then move apart with the remaining kinetic energy. One can now easily understand that all the absorption lines of the caesium atom which lie at shorter wave-lengths than 3876 Å. (higher levels than  $\text{Cs}'''$ ) may lead to this same process, since the intersections of the curves corresponding to  $ghi$  with curve  $def$  will always be lower than the levels of the excited atoms, so that in a collision with a normal atom the shaded region above  $def$  will always be reached. All these excited atoms thus give rise to the formation of a molecular ion and an electron when they collide with a normal atom. Both components of the molecular ion, the  $\text{Cs}^+$  and  $\text{Cs}$ , will begin to vibrate with respect to each other as soon as the compound is formed, since they still attract each other very strongly at point  $k$  and corresponding points (the vibrations are along the portion of the curve  $kef$ , i.e. about point  $e$ ). Thus the collision

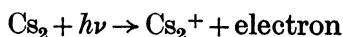
of the excited atom with a normal atom is necessary for this process before the excited atom has radiated its energy. The number of such collisions increases with increasing vapour pressure of caesium. Mohler and Boeckner as well as Freudenberg found experimentally that this photoionization at the absorption lines increases sharply with increasing pressure of caesium.

Let us now examine the absorption at the blue line 4555 Å. The  $\text{Cs}''$  formed gives rise by collision with Cs to a potential curve  $lmn$ , that is to say, to the left the energy cannot go higher than point  $o$ , so that no ionization will result. If, however, the temperature is sufficiently high both components  $\text{Cs}''$  and Cs may possess a definite kinetic energy already before the collision, so that a higher point may be reached on the potential curve. If point  $p$  is reached in this way ionization will result. Freudenberg found that by irradiation with this wave-length ionization actually did occur, but that 0.125 electron volt had to be taken up from the thermal energy of the atoms. This ionization, in contrast to that which results from absorption at shorter wave-lengths, is dependent on temperature.

The absorption of light at the red line 8521 Å. does not lead to a similar process. The corresponding point  $u$  on the curve  $rst$  lies so far above the level  $r$  that the necessary energy cannot be taken up from the thermal energy. However, according to Freudenberg, intensive irradiation with this wave-length can bring about ionization, whereby we must assume a collision between two excited atoms  $\text{Cs}'$  (level  $v$ ). The intersection of the curve  $vwy$  with  $def$  is lower than level  $v$ . In contrast to the process taking place at other absorption lines the ionization resulting from the absorption at this line is not proportional to the intensity of the light used but is proportional to the square of its intensity. The number of excited atoms increases proportionally with the intensity of the light; the number of collisions between two excited atoms increases therefore proportionally to the square of this intensity.

We have already mentioned above that light of wave-lengths lying between the absorption lines may also lead to

ionization. Boeckner and Mohler\* have shown that this is a real effect and that it may not be ascribed to imperfect action on the part of the monochromator used. This ionization effect between the absorption lines decreases with increasing temperature and may probably be ascribed to direct photoionization of  $\text{Cs}_2$  molecules. This means in Fig. 70 in connection with our discussion in §§ 54 and 55, that a transition occurs from point  $b$  to the point  $z$  vertically above  $b$  on the curve  $def$ . The direct photoionization



takes place at wave-lengths shorter than  $3800\text{\AA}$ ., a wave-length which corresponds to a distance  $bz$  of  $3.25$  electron volts. Thus absorption of light at this wave-length results *directly* in the formation of a molecular ion  $\text{Cs}_2^+$  and an electron, in which formation the components of the molecular ion still possess quite a large amount of potential energy with respect to each other, which causes them to execute vibrations with respect to each other after the process of absorption of light. That this ionization of molecules is still relatively important compared with the ionization due to excited atoms, notwithstanding the fact that there are only a few  $\text{Cs}_2$  molecules relative to the number of  $\text{Cs}$  atoms, is due to the fact that in the absorption of light by molecules *each* absorbed quantum causes ionization, whereas the excited atoms can only give ionization when they collide with an atom during the time in which they exist in the excited state.

We have gone into some detail over these processes since they offered an opportunity of considering more closely several peculiarities relating to potential curves, such as the meaning of certain intersections and the influence of thermal energy. We must note in addition that the combining energy of the  $\text{Cs}_2^+$  ion cannot immediately be derived from these processes. Freudenberg gives a value of  $1.06$  electron volts for this quantity, but this is merely the difference in level between  $p$  and  $d$ ; in his calculations no account is taken of the fact that the distance between the nuclei of the  $\text{Cs}_2^+$  molecular ion in its

\* C. Boeckner and F. L. Mohler, *Bur. Stand. J. Res.*, Wash., **5**, 831 (1930).



equilibrium position is smaller than in the  $\text{Cs}_2$  molecule. We may estimate the real combining energy of the  $\text{Cs}_2^+$  molecular ion as made up of  $\text{Cs}^+$  and  $\text{Cs}$ , at about 2.3–2.4 electron volts. In this connection the potential curves given here differ essentially from those given by Hughes and DuBridge in their well-known book.\*

### § 57. The shift of the ionization limit under the influence of electric fields.

Strong electric fields exert an influence upon the spectral lines, upon the absorption lines as well as upon the emission lines. We shall not discuss this effect—the Stark effect—here as it would lead us too far afield. It is, however, of importance

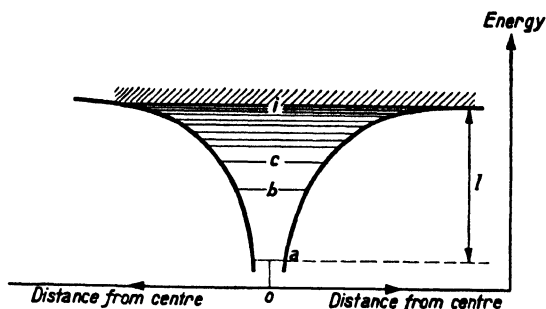


Fig. 71. Potential curves referring to the binding of an electron by the rest of the atom.

to consider what influence an electric field exerts upon the convergence limit of the line absorption spectrum of an atom. At this limit just enough energy is taken up to liberate the electron (§ 11). Just as we have seen in the case of a metal (§ 9) that the electron emission can be increased by accelerating fields due to the fact that the work function is lowered by the applied field, so we must now expect a similar phenomenon in the case of an atom. The bond of an electron with the rest of the atom can be represented as in Fig. 71 by potential curves. If we represent the energy content of an atom whose electron is in its normal orbit (normal state of the atom) by the level  $a$ , then  $b$ ,  $c$ , etc. represent the various excited states of the atom.

\* A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, p. 267 (1932).

If by absorption of light the electron is raised to the level  $i$  or higher, ionization takes place (limit of convergence of the absorption lines and adjacent region of continuous absorption). If an electric field is now applied we reach the state represented in Fig. 72. Ionization takes place already after the addition of a quantity of energy  $I'$  smaller than  $I$ . Thus one must expect that the series of absorption lines will be broken off at a certain wave-length, and that ionization already takes place at longer wave-lengths. The electron will be compelled to leave the atom in the direction of the electric field.

It has actually been found by Rausch v. Trautenberg, Gebauer and Lewin\* that in the absorption spectrum of

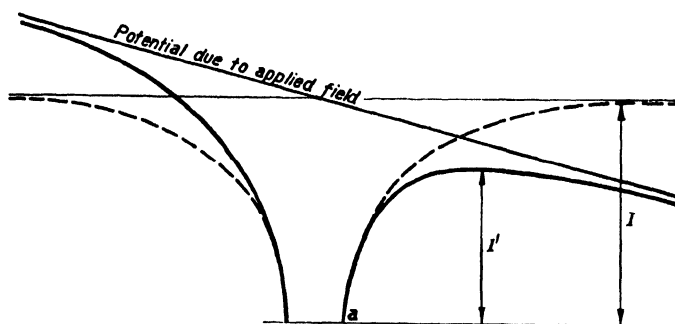


Fig. 72. Lowering of the ionization limit by an applied field.

hydrogen under very strong electric fields (more than  $10^6$  volts/cm.) the short wave-length lines no longer occur.

Potassium was investigated by Kuhn† and Bakker‡ who found in this case that even at relatively weak fields the series of absorption lines breaks off before it reaches the normal limit of convergence. In addition new absorption lines were observed which do not occur in the normal absorption spectrum (so-called forbidden lines). The ionization limit of potassium is at  $2860 \text{ \AA}$ . (4.32 volts). Bakker found that with a field of 200 volts/cm. the limit lay at  $2869 \text{ \AA}$ ., with 780 volts/cm. at  $2875.5 \text{ \AA}$ ., and with 1600 volts/cm. at about  $2880 \text{ \AA}$ . In the last

\* H. Rausch v. Trautenberg, R. Gebauer and G. Lewin, *Naturwissenschaften*, **18**, 132, 417 (1930).

† H. Kuhn, *Z. Phys.* **61**, 805 (1930).

‡ C. J. Bakker, *Proc. Roy. Acad. Amst.* **36**, 589 (1933).

case the ionization potential has been lowered from 4.32 to 4.29 volts. We shall see later (§§ 62, 65, 66, 67, 68) that with atoms of alkali metals adsorbed on fluoride, hydride or oxide surfaces the ionization limit is lowered to a much greater degree. The electric fields going out from these surfaces are much greater at the point where the atom is placed than the fields used in the experiments just discussed.

It must still be noted that when polarized light is used, and when the polarization is parallel to the electric field, the series of absorption lines breaks off at shorter wave-lengths than when the direction of polarization is perpendicular to the electric field.

## CHAPTER VIII

### THE ABSORPTION OF LIGHT BY MATTER IN THE ADSORBED STATE

#### § 58. Absorption of light and adsorption energy.

When an atom or a molecule is adsorbed on any surface, its absorption of light will usually be quite different from the absorption of the same substance in the free gaseous state. One may in general expect that the adsorption energy of the excited molecule which results from the absorption of light will be different from that of the molecule in its normal state. If in a certain process of light absorption by matter in the gaseous form, the energy absorbed is

$$h\nu = \Delta E,$$

one can easily understand that the corresponding energy for matter in the adsorbed state will be different. The latter energy can be deduced by means of an imaginary cycle as follows. The adsorbed molecule is liberated from the surface, a process requiring the adsorption energy  $Q_A$ . The molecule  $A$  is then transformed into its excited state  $A'$  by means of the energy  $\Delta E$ , and then  $A'$  is brought back to the surface, giving a gain in energy of  $Q_{A'}$ . Thus the same final state has been reached as is reached directly by the absorption of light by matter in the adsorbed state. The amount of energy taken up in the process will consequently be the following:\*

$$h\nu_{\text{ads.}} = Q_A + \Delta E - Q_{A'}.$$

In the calculation of the adsorption energy of the molecule in its excited state the Franck-Condon principle (§ 54) must be kept in mind. This can again best be made clear by means of potential curves. In Fig. 73 curve *abc* represents the potential curve of the molecule in its normal state with respect to the surface;  $Q_A$  is the adsorption energy. Curve *def* is the potential curve of the molecule in its excited state  $A'$  with respect to the

\* J. H. de Boer, *Z. phys. Chem. B*, **18**, 49 (1932).

surface, in which it is assumed that the adsorption energy  $Q_{A'}$  is smaller than  $Q_A$ , and in addition that the distance of  $A'$  to the surface at equilibrium is greater than the distance of  $A$  to the surface. In the absorption of light by matter in the adsorbed state we are concerned with the transition from  $b$  to  $g$ , whereby the excited molecule  $A'$  receives vibration energy with respect to the surface, and the amount of adsorption energy of  $A'$  to be considered ( $Q'_{A'}$ ) is less than  $Q_{A'}$ . The case represented in Fig. 73 is one of those in which the absorption

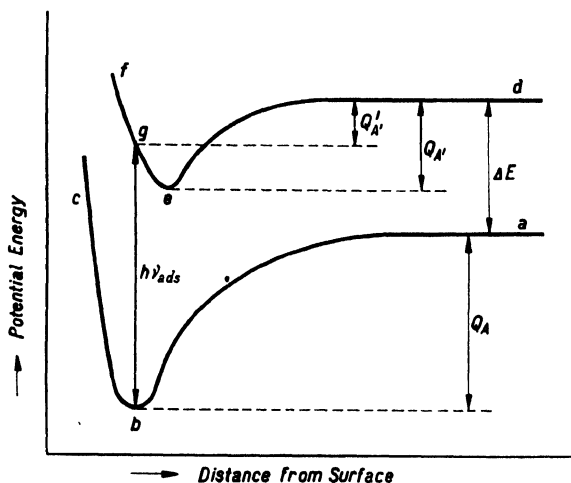


Fig. 73. Diagram showing the case in which the absorption of light by matter in the adsorbed state requires more energy than in the free gaseous state.

of light by matter in the adsorbed state requires more energy than in the free gaseous state:

$$h\nu_{\text{ads.}} > \Delta E,$$

and thus takes place at shorter wave-lengths. This is due to the fact that  $Q'_{A'}$  is smaller than  $Q_A$ . When  $Q'_{A'}$  is greater than  $Q_A$ , which case is illustrated by the potential curves in Fig. 74, the absorption of light takes place more easily by matter in the adsorbed state than in the gaseous state, and the absorption is shifted toward longer wave-lengths. Thus the problem whether  $h\nu_{\text{ads.}}$  will be greater or less than  $\Delta E$  is reduced to the question whether  $Q'_{A'}$  is greater or less than  $Q_A$ . We are therefore concerned only with  $Q'_{A'}$  and not with  $Q_A$ .

so far as the molecule in its excited state is concerned, and it may very well happen that  $Q_{A'}$  is greater than  $Q_A$ , but that because of the positions of the potential curves  $Q'_{A'}$  is less than  $Q_A$ . In such a case the adsorption energy of the excited state is greater than that of the normal state and the absorption is nevertheless shifted toward shorter wave-lengths as a result of the adsorption, since the excited molecule gains very much energy of vibration with respect to the surface by the absorption of light. It is quite probable that the adsorption of iodine on

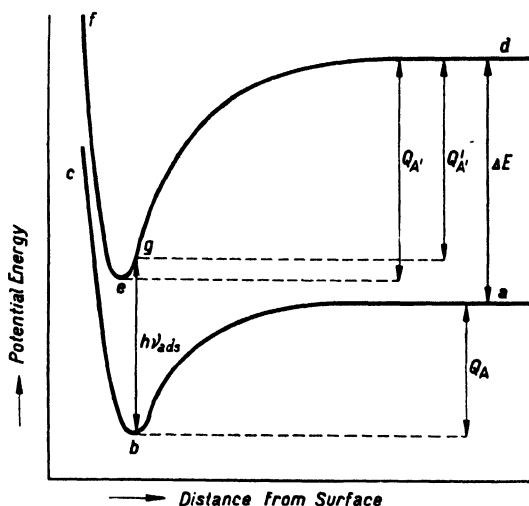


Fig. 74. Diagram showing the case in which the absorption of light by matter in the adsorbed state requires less energy than in the free gaseous state.

calcium fluoride is an example of this case.\*  $Q'_{A'}$  does not even have to have a positive value in every case; if the intersection  $g$  is higher than the level  $d$ ,  $Q'_{A'}$  is negative.

Depending thus on the value of  $Q_A$  in relation to that of  $Q_{A'}$ , the absorption of light by matter in the adsorbed state is shifted with respect to that of matter in the gaseous state, toward the red, toward the violet, or is left unchanged. One does not always observe merely a shift of the absorption band. The absorption coefficient for certain wave-lengths, which may be weak in the case of the gas, may be much greater when

\* J. H. de Boer and J. F. H. Custers, *Z. phys. Chem. B*, **21**, 208 (1933).

the substance is adsorbed, or *vice versa*, while it is quite possible that in the adsorbed state electron transitions take place which are not possible in the free gaseous state, and *vice versa* (cf. the behaviour in an electric field in § 57).

As an example of a shift of the absorption toward shorter wave-lengths we may mention here the adsorption of iodine or nickel dimethylglyoxime on calcium fluoride films; an example of a shift toward longer wave-lengths is the adsorption of *p*-nitrophenol, phenolphthalein, thymolphthalein or caesium on such salt layers as calcium fluoride or barium fluoride. We shall return later to several of these examples.

### § 59. Salt films as adsorbing surfaces.

The thin transparent films of inorganic salts as they are obtained by sublimation in a high vacuum are especially suitable for the study of the absorption of light by matter in the adsorbed state. If one sublimates calcium fluoride or barium fluoride for example in a high vacuum on a glass or quartz wall, one obtains a completely clear and invisible layer of a thickness of from 0.1 to 0.2  $\mu$ , which not only absorbs no light in the visible part of the spectrum, but is also completely transparent in the ultraviolet to very short wave-lengths. Such a film is well able to adsorb very many substances, one of which is iodine.\* In this adsorption the film becomes homogeneously coloured, so that the colour of the adsorbed material can be observed visually, and the absorption of light can also be directly measured without the hindrance of an absorption of light by the adsorbent. The study of the adsorption isotherms and the comparison of different salts with each other has shown that in the case of such salts as calcium fluoride, barium fluoride and barium chloride the negative ions exist on the outside, a fact which is probably connected with the existence of octahedron faces as limiting surfaces.† In addition the very thin films are nevertheless far from compact, but are built up of very thin

\* J. H. de Boer, *Proc. Roy. Acad. Amst.* **31**, 906 (1928); *Physica*, **8**, 145 (1928); J. H. de Boer and J. Broos, *Z. phys. Chem. B*, **13**, 134 (1931); J. H. de Boer and C. Zwikker, *Z. phys. Chem. B*, **3**, 407 (1929).

† J. H. de Boer, *Z. phys. Chem. B*, **14**, 149, 457 (1931).

laminae which are on the average only a few molecules thick.\* Optical experiments, several of which we shall discuss in the following sections, and also experiments with the help of electron reflection† have fully confirmed these results.

The optical behaviour of many substances adsorbed on other salt layers, such as sodium chloride, potassium bromide, and caesium or barium oxides, has led to the conclusion that the surface is built up of negative ions, or consists at least partially of negative ions.

In many adsorption phenomena at the most only one monomolecular adsorbed layer is formed. The adsorption of iodine for example on one of these salt films gives only a monomolecular covering.‡ The fact that nevertheless one can still see the colour of the adsorbed iodine very well, and can measure its absorption of light, is due to the laminary structure of the salt films, whereby many monomolecular layers of the adsorbed material lie one behind the other in the path of the light. If for example only 1 mg. of calcium fluoride is sublimed on 100 cm.<sup>2</sup> of glass, a salt layer is obtained which consists on the average of 12 laminae of about  $0.25 \times 10^{-6}$  cm. thickness. Thus considering the fact that there is an adsorbing surface on both sides of each lamina, there may already be 24 monomolecular adsorbed layers present one behind the other.

The magnitude of the total surface of these salt films has been determined in a few cases, for example in the case of barium chloride films by means of the reaction of alizarin, and in the case of calcium fluoride by means of the adsorption of a monomolecular layer of water. Adsorbed molecules of alizarin react under the influence of heat with the negative fluorine or chlorine ions§ of the salt surface upon which they are adsorbed. In the same way as was described in § 15 with adsorbed water molecules, in this reaction also molecules of the halogen acids

\* J. H. de Boer, *Z. phys. Chem. B*, **14**, 155 (1931); J. H. de Boer and C. J. Dippel, *Z. phys. Chem. B*, **21**, 198 (1933); J. H. de Boer and J. J. Lehr, *Z. phys. Chem. B*, **24**, 98 (1934).

† W. G. Burgers and C. J. Dippel, *Physica*, **1**, 549 (1934).

‡ J. H. de Boer, *Z. phys. Chem. B*, **15**, 300 (1932); **17**, 161 (1932); **20**, 11 (1933).

§ J. H. de Boer, *Z. phys. Chem. B*, **15**, 281 (1932).



are set free, and the residual alizarin ions remain adsorbed in the form of ions on the surface now freed of its outermost halogen ions. By determining the amount of hydrogen chloride which is freed or the amount of alizarin adsorbed, one may learn something about the magnitude of the salt surface. As was already mentioned in § 15, on some salt surfaces, that of calcium fluoride for example, the water molecules of the first monomolecular layer are bound so tightly that they cannot be removed at ordinary temperatures. By allowing caesium to react upon such a layer of adsorbed water molecules, and then determining the hydrogen or the caesium oxide formed, the magnitude of the surface may also be found.\*

As was stated above many substances are adsorbed to give a monomolecular film only. It appears that with atomic hydrogen, one atom of hydrogen at the most can be added to one fluorine ion of the surface.† In the adsorption of iodine there is at most one iodine molecule for two fluorine ions of the surface. The easily polarizable caesium atom can however be adsorbed to form a layer of more than one atom in thickness.‡

### § 60. Sintering and swelling of salt layers.

If the salt is always sublimed in a high vacuum in the same way, the specific surface is also always practically the same (with calcium fluoride about  $2.4 \times 10^6$  cm.<sup>2</sup>/gram); the surface is thus proportional to the amount of salt sublimed. The laminated surface has in addition many active spots (corners and edges of the laminae).

By heating at temperatures between 150 and 350° C. a decrease in the surface takes place due to sintering, to a definite degree for each temperature.§ During this sintering process the salt films remain completely clear. The laminae merely

\* J. H. de Boer and C. J. Dippel, *Z. phys. Chem. B*, **25**, 399 (1934). In this latter case some new experiments of C. J. Dippel show that the water molecules in several cases cover only a part (about  $\frac{1}{3}$ ) of the surface, probably only active places.

† J. H. de Boer and J. J. Lehr, *Z. phys. Chem. B*, **22**, 423 (1933); **24**, 98 (1934).

‡ J. H. de Boer and C. J. Dippel, *Z. phys. Chem. B*, **21**, 278 (1933).

§ J. H. de Boer and C. J. Dippel, *Z. phys. Chem. B*, **21**, 198 (1933).

become more or less firmly attached to each other, so that the interlaminary surface is considerably decreased, and moreover a number of active spots disappear. In the adsorption of iodine not only is the amount adsorbed actually very much decreased after sintering has taken place, but the shape of the isotherm is also changed in such a way that it must be concluded that the number of active spots that have disappeared is large compared to the decrease in total surface.

While the laminae after the sintering lie with their surfaces together, they do not grow together to form one crystal lattice. Thus the forces which hold the surfaces of the laminae together after sintering are considerably smaller than the forces which act *within* the salt lattice; they may rather be compared to the forces between the various layers of a layer lattice. Molecules or atoms which are especially strongly adsorbed are able to overcome these forces again, and to abrogate the effect of the sintering. Thus for example a film of calcium fluoride, which has been sintered at temperatures not higher than 350° C. and whose surface has become so small that practically no adsorption of iodine can be measured, is again completely broken up by the adsorption of caesium.\* Thus caesium works its way between the laminae and pushes them away from each other again. One may consider therefore that a sintered calcium fluoride film swells in caesium in the same way that gelatine swells in water when the gelatine micelles are pushed away from each other by the strong adsorption of water.

If after the swelling of the sintered calcium fluoride layer in caesium, the caesium is removed at a relatively low temperature, the broken up state of the film continues to exist. One can for example measure once more the original value for the adsorption of iodine, which is a sign that the surface is again just as large as it was before the sintering was performed. The swelling of the layer in caesium has thus completely destroyed the effect of the sintering.

\* J. H. de Boer and C. J. Dippel, preliminary notice: *Chem. Weekblad*, **30**, 78, 221 (1933); detailed publication to appear shortly in *Rec. Trav. chim. Pays-Bas*.

If the sintering is carried out at higher temperatures (above  $350^{\circ}\text{C}.$ ), then the lamina surfaces become more and more tightly attached to each other, and caesium can no longer remove the effect of the sintering. A similar case is found in the swelling of gelatine in water; if by means of a heat treatment one makes the mutual bonds between the micelles stronger, the capacity of the gelatine to swell in water decreases.\*

The alkali metals such as caesium, rubidium and potassium are also able to cause such a swelling in other cases. They may penetrate into a lattice of graphite and take up places between the monatomic carbon layers† which are piled one upon the other in graphite in the direction of the hexagonal axis. In this case again caesium destroys the weaker bond *between* the atomic carbon layers, while it leaves the hexagonal arrangement *within* the layers intact. The only difference between this case and that with calcium fluoride is that with calcium fluoride the adsorption takes place between the laminae, while with graphite it takes place between layers which are one atom thick. Because of this latter fact the swelling of graphite leads to a stoichiometric compound; at first  $\text{C}_{16}\text{Cs}$ , or  $\text{C}_{16}\text{K}$  as the case may be, is formed (dark blue in colour), then  $\text{C}_8\text{Cs}$  or  $\text{C}_8\text{K}$  (shiny copper-coloured).‡ The swelling of sintered calcium fluoride films in caesium is therefore more nearly analogous to that of gelatine in water than to the swelling of graphite.

Layers of barium fluoride and barium chloride are more easily sintered than those of calcium fluoride, while layers of alkali halides are still more easily sintered. A film of sodium bromide exhibits the phenomenon of gradual sintering when it is merely kept at room temperature. In this case the opening up of the surface is also easier; iodine, which is less strongly adsorbed on the surface than caesium, is able to open up the sintered layer of sodium bromide. In this case the opening up

\* J. H. de Boer and C. J. Dippel, *Rec. Trav. chim. Pays-Bas*, **52**, 222 (1933).

† A. Schleede and M. Wellmann, *Z. phys. Chem. B*, **18**, 1 (1932); U. Hofmann and A. Frenzel, *Kolloidzshr.* **58**, 8 (1932).

‡ K. Fredenhagen and G. Cadenbach, *Z. anorg. Chem.* **158**, 249 (1926).

leads finally to a complete rearrangement; new crystallites are formed, in other words, recrystallization takes place.\* The adsorption of iodine may under certain circumstances cause a partial opening up of sintered calcium fluoride layers.

### § 61. The absorption of light by adsorbed iodine.

When iodine is adsorbed on a layer of calcium fluoride prepared in high vacuum by sublimation, at very small surface concentrations only the most active spots on the surface are occupied. As has already been mentioned in § 59 the laminated salt layer possesses a large number of very active spots (corners and edges of the laminae), which decrease (§ 60) in number and in activity more quickly by sintering than the total surface decreases in size. The electrostatic fields of these very active spots are so strong that the electrostatic polarization exceeds by far the van der Waals adsorption forces (cf. § 16), so that at these active spots adsorbed molecules or atoms will have a directed, induced dipole.

When at higher surface concentrations the less active spots of the salt surface are also occupied by adsorbed molecules, the van der Waals forces are in the end the most important for the binding of these molecules to the surface.†

Thus when only a few iodine molecules are adsorbed ( $\theta$  values of a few per cent. at the most), the state of combination of the iodine may be compared with that of an iodine molecule bound to an iodine ion in the triiodide ion ( $I_3^- = I^- \cdot I_2$ ). At greater values of  $\theta$  however the bond of the iodine molecule, which is held adsorbed only by the van der Waals forces, must be compared to the state of combination occurring in solid iodine where the lattice is also built up only by means of the van der Waals forces.

The absorption spectra of iodine adsorbed on a layer of calcium fluoride do actually show that this view is correct.‡ When only a very small amount of iodine is adsorbed ( $\theta < 0.001$ )

\* J. H. de Boer and J. F. H. Custers, to be published in *Rec. Trav. chim. Pays-Bas*.

† J. H. de Boer and J. F. H. Custers, *Z. phys. Chem. B*, **25**, 225 (1934).

‡ J. H. de Boer and J. F. H. Custers, *Z. phys. Chem. B*, **21**, 208 (1933).

an absorption spectrum is obtained such as is represented by curve *a* in Fig. 75. At this surface concentration the adsorbed layer (room temperature) is in equilibrium with iodine cooled to  $-83^{\circ}\text{C}$ . At higher surface concentrations the total absorption of light naturally increases, but it increases less than would correspond with the increased amount of adsorbed iodine. At the same time the character of the absorption curves is modified, the maxima are much less sharp and pronounced, and especially at the long wave-length end the absorption increases.

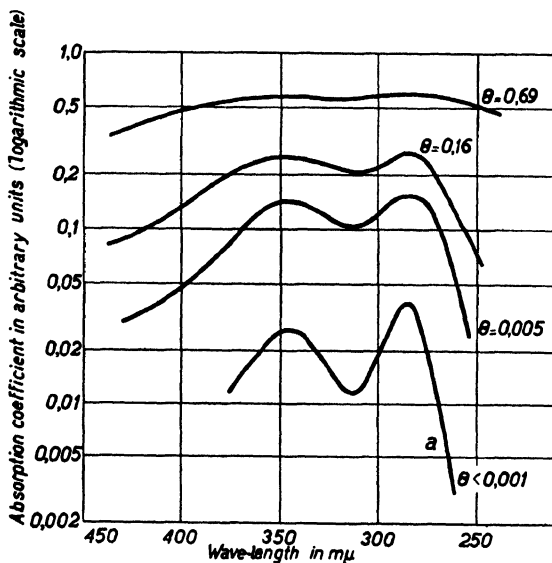


Fig. 75. Absorption curves for iodine, adsorbed on a  $\text{CaF}_2$  surface at different values of  $\theta$ .

At the same time part of the visible spectrum is absorbed, and the adsorbed layer becomes brown in colour. The first iodine molecules adsorbed are quite colourless to the eye. The curves in Fig. 75 are drawn to a logarithmic scale, so that if the absorption were qualitatively the same at greater values of  $\theta$ , the curves would be parallel.

Thus during the building up of the adsorbed layer the character of the light absorption changes. In addition the intensity of the absorption changes also. If the absorption per molecule is calculated it appears that the molecules added at the active spots possess a much larger absorption coefficient in

this region of the spectrum than the molecules which are bound only by the van der Waals forces. In Fig. 76 the absorption

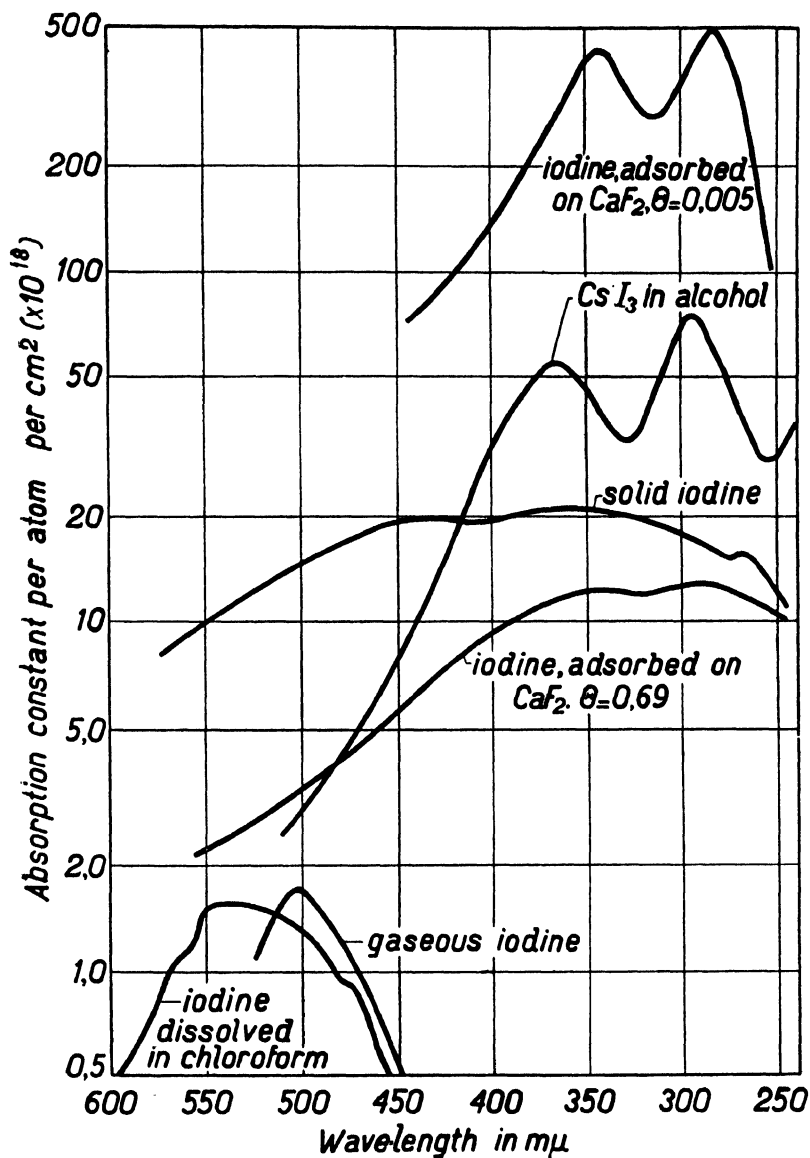


Fig. 76. Absorption of light by iodine in different states.

constant per atom per cm.<sup>2</sup> (i.e. calculated for a concentration of one atom of iodine per cm.<sup>2</sup> cross-section of the beam of

light) is represented for various states of the iodine. The curve for iodine adsorbed on the most active spots of the calcium fluoride cannot be represented, since the amount adsorbed in that state is too small to be determined; the absorption constant for the maxima of that state is certainly more than  $1000 \times 10^{-18}$ .

One may see from the figure that the iodine adsorbed at the active spots of the salt surface corresponds very well to the iodine bound to an iodine ion\* and that further the iodine adsorbed only by means of the van der Waals forces exhibits an absorption curve which corresponds to that of solid iodine. One might still further be inclined to conclude from the figure that the electrostatic fields at the most active spots are somewhat stronger than that of the iodine ion. The increase in absorption shown by the  $I_3^-$  ion for wave-lengths shorter than  $250m\mu$  may be ascribed to the absorption of the  $I^-$  ion.

With regard to the meaning of the two maxima, it can here only be noted that they are probably connected with the dissociation of the adsorbed molecule into two normal (adsorbed) atoms (maximum at the long wave-length side) or into one normal and one excited atom (maximum at the short wave-length side).†

The absorption of light by bromine molecules adsorbed at the active spots of a calcium fluoride surface is in complete agreement with this view.‡

## § 62. The absorption of light by adsorbed caesium.

As with iodine the absorption of light by caesium adsorbed on a layer of calcium fluoride varies greatly for atoms which are bound to the active spots of the surface and those which are bound to the less active spots at greater surface concentrations. Here again one would, as a first approximation, expect a correspondence between the absorption spectrum of the adsorbed caesium which is bound by van der Waals' forces,

\* Curve taken from the results of F. L. Gilbert, R. R. Goldstein and T. M. Lowry, *J. chem. Soc. Lond.* p. 1092 (1931).

† J. H. de Boer and J. F. H. Custers, *Z. phys. Chem. B*, **21**, 217 (1933).

‡ J. F. H. Custers and J. H. de Boer, *Physica*, **1**, 265 (1934).

and the absorption spectrum of solid caesium, while the absorption spectrum of the caesium adsorbed at the active spots should be quite different. As a matter of fact this is found to be the case.\* In Fig. 77 curve *a* gives the absorption spectrum for small values of  $\theta$ , while curve *b* gives the absorption for large values of  $\theta$ . At high surface concentrations the layer of caesium adsorbed on calcium fluoride is blue,† while the adsorbed layer at these concentrations finally becomes more than one atom thick.‡ The absorption spectrum of these blue layers which already possess electrical conductivity (absorption in

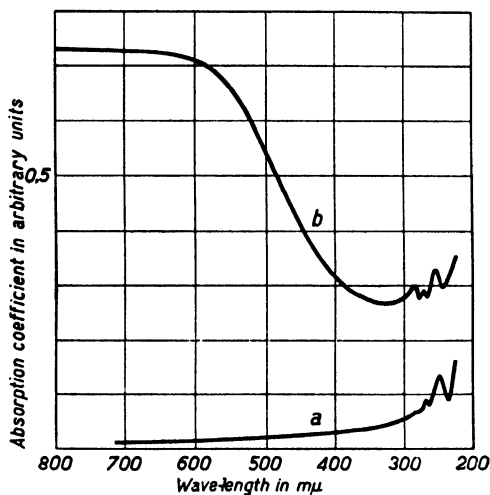


Fig. 77. Absorption of light by caesium: (*a*) adsorbed on the active places of a  $\text{CaF}_2$  surface; (*b*) adsorbed on  $\text{CaF}_2$ , at greater values of  $\theta$ .

the red and adjoining infrared) actually does correspond to the absorption of thin layers of solid caesium.§

The increasing absorption toward shorter wave-lengths, which was also present at very small surface concentrations, continues to exist at the greater surface concentration, and is superposed upon the absorption of the atoms which are less influenced electrostatically. The absorption of light by the

\* J. H. de Boer, J. F. H. Custers and C. J. Dippel, *Physica*, **1**, 935 (1934).

† J. H. de Boer and M. C. Teves, *Z. Phys.* **65**, 489 (1930).

‡ J. H. de Boer and C. J. Dippel, *Z. phys. Chem. B*, **21**, 278 (1933).

§ R. W. Wood, *Phys. Rev.* **44**, 353 (1933).



caesium atoms adsorbed on the active spots of the surface, can be considered as an ionization band of caesium which has been shifted toward longer wave-lengths.\* We have already stated in § 57 that in electric fields the ionization limit of an atom may be displaced in the direction of longer wave-lengths; in the case now under consideration the strong electric fields of the active spots on the surface also exert this action. This influence can however be more clearly recognized if potential curves are drawn as was done in § 58 for adsorbed atoms. Fig. 78 gives

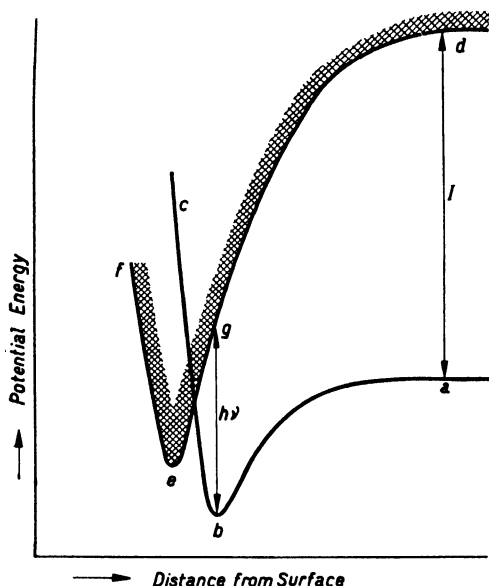


Fig. 78. Potential curves for the adsorption of a caesium atom and a caesium ion on an active spot of a  $\text{CaF}_2$  surface.

the potential curves for the case of the adsorption of caesium on calcium fluoride.† The absorption of light in the free, unadsorbed state requires the taking up of the ionization energy  $I$  in order to lead to ionization. Since a positive  $\text{Cs}^+$  ion results from the ionization and since the outside surface of the salt is covered with negative ions (§ 59), the positive ions are especially strongly bound by the projecting fluorine ions at the active

\* J. H. de Boer and M. C. Teves, *Z. Phys.* **73**, 192 (1931).

† J. H. de Boer, *Chem. Weekblad*, **29**, 34 (1932); J. H. de Boer and M. C. Teves, *Z. Phys.* **83**, 521 (1933).

spots of the calcium fluoride surface. The result is naturally that the adsorption curve of the ions (*def* in Fig. 78) has a very sharp minimum. The transition from *b* (adsorbed atom) to point *g* of the ionic adsorption curve (Franck-Condon principle, § 54) necessitates therefore very much less energy than the transition in the unadsorbed state. One can estimate that at these active spots of the calcium fluoride caesium can be ionized already by irradiation with light of a wave-length of 7000 Å. At the somewhat less active spots the ionization is also shifted somewhat less toward long wave-lengths, and we may consider that curve *a* of Fig. 77 is obtained by the superposition of photoionization curves of various caesium atoms which are adsorbed on active spots of differing activity. The photoionization thus takes place at relatively long wave-lengths, because of the fact that the ion which is formed is so strongly bound ( $Q_{A'} > Q_A$ , see § 58).

Only when caesium atoms are bound at less active spots too, and a continuous, conducting layer is formed, do we obtain the absorption curve *b* of Fig. 77, and the adsorbed caesium layer acquires a beautiful blue colour. On other fluorides also ( $\text{BaF}_2$ ,  $\text{NaF}$ ) and on oxides ( $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ ) the colour of caesium is blue at large values of  $\theta$ . On chlorides a more greyish tint is obtained. Other alkali metals have less distinctly beautiful colours\* on these salt layers; rubidium is greyish blue on calcium fluoride, potassium grey, and sodium reddish brown.†

### § 63. The absorption of light by adsorbed phenols.

The adsorption of polar substances with the dipole situated peripherally such as the phenols, takes place in a somewhat different manner from the adsorption of dipole free molecules or atoms, whose absorption of light we have just discussed in §§ 61 and 62. As was stated in § 15, in the adsorption of such dipole substances the active spots of the surface are of less importance. In this case we must consider the circumstance that with the salt layers discussed in this chapter the outside surface is composed of negative ions. The dipoles of the OH

\* J. H. de Boer and M. C. Teves, *Z. Phys.* **65**, 492 (1930).

† J. H. de Boer and W. de Groot, *Z. techn. Phys.* **12**, 303 (1931).

groups take up positions contiguous to the negative ions while the phenyl groups lie flat on the surface.\* At large surface concentrations it is possible that the phenyl groups take up positions parallel to each other through their mutual attraction and turn away from the surface,† as is the case in the adsorption of fatty acids on water surfaces. If however in order to bring this about, it should be necessary for large dipole moments to be similarly oriented, as with paranitrophenol,‡ it would require too much energy, and even at larger values of  $\theta$  the molecules remain adsorbed with their phenyl groups flat on the surface. In the case of orthonitrophenol a parallel orientation of the molecules can take place with the phenyl groups away from the surface.

Upon the first layer of the adsorbed nitrophenol molecules a second layer can be adsorbed, which is bound to the first by van der Waals' forces. In the first layer the OH groups are bound to the negative ions of the salt surface; this is not so in the second layer. Due to this influence upon the OH group the absorption spectrum is displaced toward longer wave-lengths.

The fact that this displacement toward longer wave-lengths takes place is easy to understand on the basis of an analogy with salt formation. Free, molecular paranitrophenol has an absorption maximum at  $316\text{m}\mu$ ; if paranitrophenol is dissolved in alkali thus forming *p*-nitrophenolate ions, the maximum of the absorption band is shifted to  $400\text{m}\mu$ , and the solution is yellow (*p*-nitrophenol is an indicator in analytic chemistry). If one does not remove the hydrogen ion from the OH group (as is done in salt formation) but decreases its action by adding the OH group to the outermost fluorine ions of the calcium fluoride, then a displacement of the absorption also takes place,§ in this case to  $365\text{m}\mu$ , and the adsorbed layer is also yellow.

If the absorption spectrum is measured for increasing values of  $\theta$ , it appears that the maximum at small values of  $\theta$  lies at

\* J. H. de Boer and J. F. H. Custers, *Z. phys. Chem. B*, **25**, 225 (1934).

† J. H. de Boer and C. J. Dippel, *Z. phys. Chem. B*, **25**, 408 (1934).

‡ J. H. de Boer, *Z. phys. Chem. B*, **17**, 161 (1932).

§ J. H. de Boer, *Z. phys. Chem. B*, **16**, 403 (1932).

365  $m\mu$ , and is shifted with increasing  $\theta$  toward shorter wave-lengths until it finally remains constant at 316  $m\mu$ .\* Analysis of these curves showed that each curve can be divided into two parts, of which one is similar to the absorption spectrum of unmodified *p*-nitrophenol and must be ascribed to the *p*-nitrophenol adsorbed in the second layer. The other part is due to the optically modified *p*-nitrophenol in the first adsorbed layer which is added directly on the salt surface.

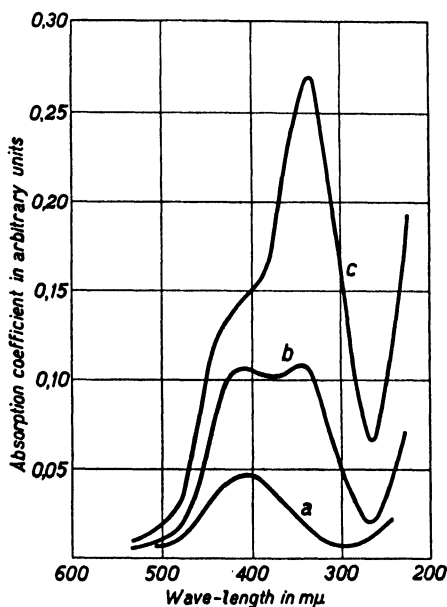


Fig. 79. Absorption of light by paranitrophenol, adsorbed on a  $BaF_2$  surface.  $\theta$  value in *c* greater than in *b*, and this greater than in *a*.

The second layer begins to be formed already when still only a fraction of the first layer is occupied (which fact can be deduced from the curves).

The examination of the absorption spectra of *p*-nitrophenol adsorbed on barium fluoride layers has confirmed the above conclusions very nicely.†

On barium fluoride the absorption maximum was shifted further toward longer wave-lengths than on the calcium fluoride surface; *p*-nitrophenol on barium fluoride has an

\* J. H. de Boer and J. F. H. Custers, *Z. phys. Chem. B*, **25**, 238 (1934).

† J. F. H. Custers and J. H. de Boer, will appear in *Physica*, **2** (1935).

absorption maximum at  $413\text{m}\mu$ . With increasing concentration a second layer is here also adsorbed, and for a certain time two maxima next to each other are obtained (Fig. 79).

Other phenolic indicators show a similar optical behaviour. The colourless thymolphthalein for example is brownish yellow when adsorbed on calcium fluoride.\* If one allows water vapour to react upon this adsorbed layer, the colour

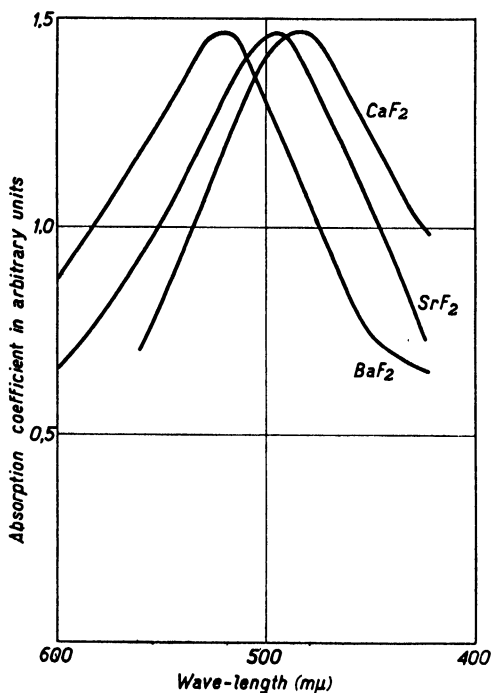


Fig. 80. Absorption spectra of alizarin, after it has reacted chemically with the surfaces of  $\text{CaF}_2$ ,  $\text{SrF}_2$  or  $\text{BaF}_2$ .

disappears since the water molecules displace the thymolphthalein molecules from the surface. By re-evacuation the brownish-yellow colour can be brought back once more. The shift of the maximum is in this case also not so great as in salt formation; thymolphthalein in alkali is blue. Phenolphthalein on calcium fluoride has an absorption maximum at  $475\text{m}\mu$ , on barium fluoride at  $536\text{m}\mu$ .\*

\* J. H. de Boer, *Z. phys. Chem. B*, **18**, 50 (1932).

In § 59 it was stated that alizarin can react in the same way as water (§ 15) with the halogen ions of the surface, whereby the corresponding halogen acid escapes, and the remaining alizarin ions are bound to the calcium ions of the resulting surface. In this case again the absorption spectrum varies greatly according to whether the alizarin ions are adsorbed on  $\text{Ca}^{++}$ ,  $\text{Sr}^{++}$  or  $\text{Ba}^{++}$  ions. Since an alizarin ion (solution in alkali) is blue, and an alizarin molecule is yellow-orange, we know that under the influence of the positive hydrogen ion the absorption band is shifted toward the violet. We must therefore also expect that the absorption band of the alizarin ion on the  $\text{Ca}^{++}$  ions of the resulting calcium fluoride surface will be at shorter wave-lengths than on the  $\text{Sr}^{++}$  ions of the resulting strontium fluoride surface, or than on the  $\text{Ba}^{++}$  ions of the resulting barium fluoride surface. The radius of the  $\text{Ca}^{++}$  ion is less than that of the  $\text{Sr}^{++}$  ion, and the latter is again less than that of the  $\text{Ba}^{++}$  ion, so that the electrostatic action decreases in the order  $\text{Ca}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$ . As a matter of fact the colour after the reaction on calcium fluoride is red, on strontium fluoride reddish violet, and on barium fluoride bluish violet. The absorption maxima are, on calcium fluoride at  $482\text{m}\mu$ , on strontium fluoride at  $495\text{m}\mu$  and on barium fluoride at  $520\text{m}\mu^*$  (Fig. 80).

#### § 64. The selective absorption of plane polarized light.

When an atom or a molecule is adsorbed on a surface, it may be expected that the system will be anisotropic. The adsorbed atom is of course under an unsymmetrical influence, and it is quite probable that its properties in the direction in which the adsorptive binding forces act should be different from its properties in directions perpendicular to this direction. The selective photoelectric effect which we met with in Chap. v in the adsorption of alkali metal *atoms* on metal surfaces, and which will be discussed in more detail in Chap. ix for the case of the adsorption of alkali metal atoms on salt (oxide) layers, shows that there is a great difference in action between polarized light whose electric vector has a component perpendicular to

\* J. H. de Boer, *Z. phys. Chem. B*, 15, 281 (1932).

the surface ( $\parallel$  light, see § 40), and polarized light whose electric vector possesses no such component ( $\perp$  light). We shall see that in each of these cases the photoelectric emission may be ascribed to a photoionization of the adsorbed atoms, and is thus caused by absorption of light by these atoms (§§ 62, 65, 71). On the basis of this it is reasonable to expect that such adsorbed atoms will exhibit a selective absorption of light, in other words, that they will absorb polarized light whose direction of vibration is such that the electric vector has a component parallel to the bond between the atom and the surface, but that they will not absorb polarized light whose electric vector has no such component. Such a selective absorption of light has actually been observed in several cases.

Fleischer\* measured the absorption of light by thin layers of potassium in variously polarized light, and also the absorption of these layers after the reaction with atomic hydrogen had formed a very thin, invisible film of hydride. We shall see later (§ 66) that in the latter case potassium atoms are adsorbed on top of the invisible hydride films. These adsorbed atoms exhibit a selective absorption. Fig. 81 shows that an absorption maximum for  $\parallel$  light is found at  $436\text{m}\mu$ , which does not appear for  $\perp$  light. Thus a selective maximum due to the potassium atoms adsorbed on the hydride film is superposed upon the light absorption of potassium. This proves that these atoms absorb only that light whose electric vector has a component perpendicular to the surface, or in other words, a component in the same direction as that of the bond between the adsorbed atom and the surface.

If the photoelectric current is now measured it appears that a sharp selective maximum is found in  $\parallel$  light at  $436\text{m}\mu$ , which maximum corresponds exactly with the selective absorption maximum (§ 66).

Another investigation directly connected with phenomena under consideration here was carried out by Fleischmann† in Pohl's laboratory in Göttingen. Thin layers of alkali metals

\* R. Fleischer, *Ann. Phys.*, Lpz., **82**, 75 (1927).

† R. Fleischmann, *Naturwissenschaften*, **19**, 816 (1931); *Nachr. Ges. Wiss. Göttingen*, p. 252 (1931).

were deposited on plane quartz plates. In light falling perpendicularly upon the plates the layers are scarcely visible; in light falling diagonally upon the plates the layers have distinct colours: sodium and potassium yellow (absorption of the violet), rubidium red (absorption of the blue-green) and caesium blue (absorption of the red) (cf. also § 62). Thus apparently these layers only absorb light when its electric vector has a component perpendicular to the surface. When polarized

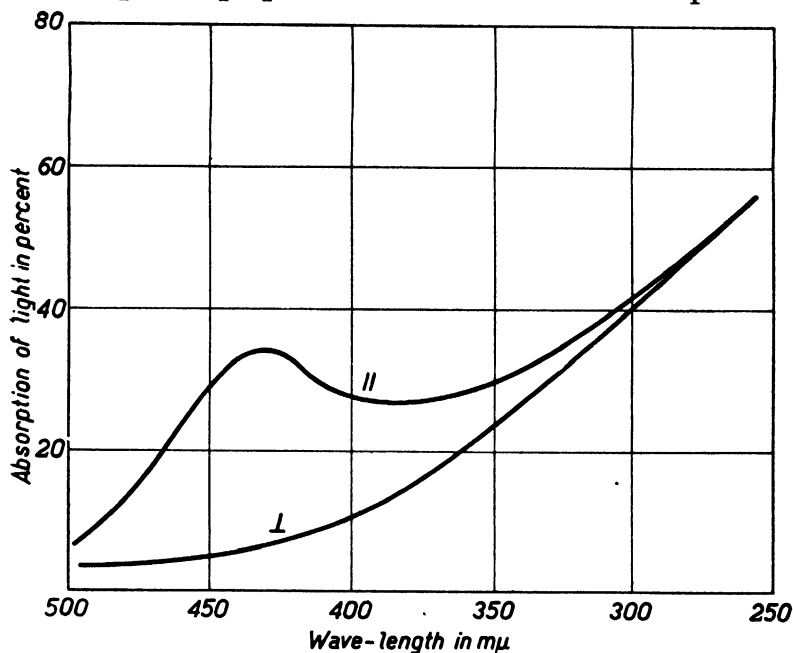


Fig. 81. Absorption of  $\parallel$  and  $\perp$  polarized light by potassium atoms adsorbed on a potassium hydride covered potassium layer. Angle of incidence  $45^\circ$ . According to R. Fleischer, *Ann. Phys., Lpz.*, **82**, 75 (1927).

light is used the effect is much stronger; the layers are then strongly dichroic. The measurements of the absorption spectra showed that only in  $\parallel$  light could a pronounced absorption band be obtained; in  $\perp$  light no absorption was found. In Fig. 82 the absorption curve of potassium on quartz is given, measured in  $\parallel$  light at an angle of incidence at  $55^\circ$ .

Closely connected with our problem are the detailed investigations by Weigert\* and his coworkers of photodichroic

\* Several summaries, F. Weigert, *Naturwissenschaften*, **9**, 583 (1921); **16**, 613 (1928); **19**, 969 (1931); *Photogr. Korrespondenz* 1934, Beilage VI.



phenomena. Although these investigations are concerned with a subject quite different from that of this book, we should like to give very briefly a few of the results which are of some importance to us here. About 1919 Weigert discovered that photographic plates, suitable for direct copying, which had already been coloured to a certain degree by exposure to light, became strongly dichroic upon subsequent exposure to polarized light. It was already known of such layers that they show the phenomenon of "colour adaptation", that is to say that after irradiation with red light they transmit red light more easily, after irradiation with blue light they become

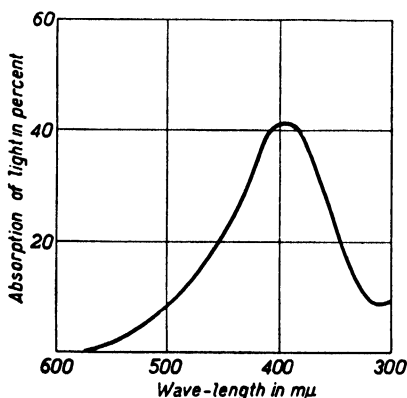


Fig. 82. Selective absorption of  $\parallel$  light by a thin potassium layer.  
R. Fleischmann, *Nachr. Ges. Wiss. Göttingen*, p. 255 (1931).

themselves blue, or in other words they transmit blue light. Light of a definite frequency has thus such a bleaching action, that this frequency is transmitted more easily (see also § 86). Weigert now found that by the use of polarized light with a certain direction of vibration the process of bleaching takes place in such a way that thereafter the transmission of light of that particular vibration direction is increased, while the transmission of light of the same frequency but with a direction of vibration perpendicular to the former is not increased.\* By means of a photochemical reaction (bleaching) with polarized light a dichroic system has been formed from an originally optically isotropic system.

\* F. Weigert, *Ann. Phys., Lpz.*, **63**, 681 (1920).

In addition to this primary photodichroism, induced photodichroism was later discovered.\* It appeared that by irradiation by polarized light of a previously unexposed plate a latent image was formed which upon being developed gave a dichroic silver layer. Thus in this phenomenon the reduction of the silver halide by the developer is induced in an oriented manner.

According to the original conception of Weigert the polarized light changes the originally isotropic units to units with a preferential direction. The absorbing centre is in this case a silver atom which forms, together with other silver atoms, silver halide molecules, gelatine and water, a "micelle" held together by van der Waals' forces. This micelle has a spherical structure with no preferential direction.† In the absorption of light work would be performed against the van der Waals forces, and if polarized light were used the work would be performed in a definite direction.

This view does not tally with that which we discussed at the beginning of this section, according to which we should rather expect that in a system like that of a photographic emulsion, adsorbed atoms or molecules would exist, the direction of whose bond with the surface upon which they are adsorbed would take all possible positions. One would expect that upon exposure to polarized light only those atoms or molecules, the direction of whose bond corresponds to the electric vector of the active light, would absorb that light and be changed photochemically. The resulting system would then indeed be dichroic.

On the basis of later experiments Weigert also came to the same conclusion. When a photographic emulsion is first exposed to polarized light, and the resulting silver is removed with chromic acid, then after re-exposure, this time to non-polarized light, and developing, a dichroic silver layer is formed. It appears in this process that of the non-polarized light only that is absorbed whose direction of vibration is per-

\* F. Weigert, *Naturwissenschaften*, **16**, 613 (1928); *Z. phys. Chem. B*, **3**, 377 (1929); **4**, 83 (1929).

† Cf. F. Weigert, *Z. phys. Chem. B*, **10**, 241 (1930).

pendicular to the direction of vibration of the previously used polarized light.\*

It was found further, that in the congealing of silver halide gelatine emulsions, thin superficial layers are formed on the surface which can easily be brushed off and are less than  $780 \text{ \AA}$ . in thickness, and which may have a very large red sensitivity.† This layer consists of a great number of elementary micelles parallel to each other, which only absorb that light whose electric vector has a component perpendicular to the surface. Thus light falling perpendicularly upon this layer is not absorbed. If the plate is made slightly damp a partial disorientation of the superficial layer occurs and light falling perpendicularly upon it is then partially absorbed.‡

We may thus conclude that the absorbing molecules, which are adsorbed on the surfaces of the gelatine micelles or on the silver halide crystals, exhibit a selective absorption for light polarized in a definite plane. It is somewhat difficult in these cases to say exactly which is the absorbing atom or molecule. According to Weigert's§ views the absorption of light is in the first instance due to silver atoms, even with unexposed plates, in which there is always a small quantity of very small silver particles present.

Not only photographic emulsions but also very many dyes deposited on collodion or gelatine films show the phenomenon of primary dichroism.|| Apparently the molecules of many dye-stuffs which are adsorbed on the surfaces of the colloidal units of the collodion or gelatine films absorb light of a certain direction of vibration selectively.

\* F. Weigert and F. Stiebel, *Naturwissenschaften*, **19**, 108 (1931).

† F. Weigert and F. Stiebel, *Z. phys. Chem. B*, **16**, 118 (1932).

‡ F. Weigert and E. Eberius, *Kolloidzshr.* **58**, 276 (1930); **60**, 13 (1932).

§ Cf. F. Weigert, *Z. wiss. Photogr.* **29**, 191 (1930).

|| F. Weigert and M. Nakashima, *Z. phys. Chem. B*, **4**, 258 (1929); **7**, 25 (1930); T. Kondo, cited by F. Weigert, *Z. wiss. Photogr.* **30**, 217 (1930).

## CHAPTER IX

### THE SELECTIVE PHOTOELECTRIC EFFECT

#### § 65. The adsorption of caesium on fluoride layers.

In § 62 we have seen that the absorption spectrum of caesium atoms adsorbed on the most active spots of a layer of calcium fluoride, which has been formed by sublimation in a high vacuum, is quite different from that of the caesium atoms adsorbed at high surface concentrations. At small values of  $\theta$  the adsorbed atoms do not form a continuous monatomic layer of caesium, so that they also fail to exhibit the properties of a metal, such as metallic lustre or electrical conductivity. The lack of metallic conduction electrons is further manifested in the absorption of light; the blue colour which is later assumed by the caesium at higher surface concentrations is still wanting (cf. curve *a* of Fig. 77 in § 62). Illumination of the surface when it is in this condition (small values of  $\theta$ ) causes it to emit electrons. Thus the layer of calcium fluoride covered with isolated atoms of adsorbed caesium forms a photoelectrically active surface. We have already seen in § 62 that the absorption of light by these individually adsorbed caesium atoms must be considered to be a photoionization which has been shifted toward longer wave-lengths by the action of the electric field of the active spots of the surface. Because of the fact that the caesium ions which result from the ionization are bound so much more strongly to the active spots of the calcium fluoride than the caesium atoms themselves, the ionization limit is at much longer wave-lengths than that of the free caesium atoms. On the basis of the absorption spectrum of Fig. 77 in § 62 it may be expected that photoemission can be attained already by illumination with light of a wave-length of 7000 Å.

In order to obtain a continuous current upon continuous illumination, the caesium ions formed on the surface by photoionization must be neutralized to be able to emit their electrons again in a direction away from the surface. This neutralization which serves to bring about a steady supply of electrons to be

emitted may occur through the calcium fluoride layer when the calcium fluoride layer itself is deposited on a metallic base. The supporting metal thus finally furnishes the electrons destined for emission.

It appears experimentally\* that if one sublimates a very thin layer of calcium fluoride on a supporting metal, silver for example, which as a cathode can be made negative with respect to an anode, and then allows caesium to be adsorbed on this calcium fluoride layer, a photocathode is obtained. The photocurrent measured increases as a function of the time of exposure to a steady supply of caesium (i.e. as a function of the fraction of the surface covered,  $\theta$ ), until a maximum is reached, whereafter the current decreases until it reaches a constant value (Fig. 83). During the rise of the current the salt layer is not yet coloured blue by the adsorbed caesium; at the maximum the blue coloration begins to be noticeable; the part of the curve in Fig. 83 which represents the falling current and especially the subsequent horizontal part of the curve corresponds to a steady intensification of the blue colour.

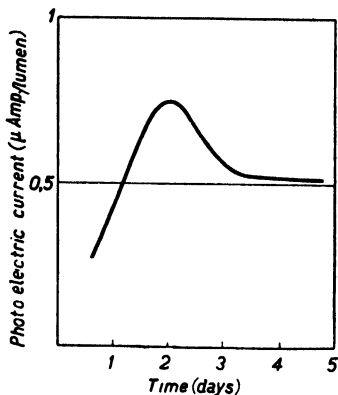


Fig. 83. Variation of photoelectric current with the amount of Cs atoms, adsorbed on a  $\text{CaF}_2$  layer.

As can be seen from the figure, during the building up of the adsorbed layer, while  $\theta$  is still small, the measured photocurrent increases approximately linearly with  $\theta$ . The relation here is different in principle from that in the adsorption on *metals* (see § 40), where we have seen that the *logarithm* of the photocurrent increased about proportionally with  $\theta$ . This difference is due to the fact that in this case the mechanism of the emission is actually quite different. For example, in the adsorption of caesium on metals the work function is lowered by the caesium *ions*, and the lowering  $\Delta\phi$  is proportional to  $\theta$ . Since in addition the logarithm of the electron emission varies

\* J. H. de Boer and M. C. Teves, *Z. Phys.* **65**, 489 (1930).

proportionally with  $\Delta\phi$ , the above-mentioned logarithmic relation becomes clear (see also § 40). In the adsorption on salt layers (and corresponding cases of adsorption of *atoms*) the adsorbed *atoms* themselves are the source of the emitted electrons, and the photocurrent is thus proportional to the number of adsorbed atoms.

Our knowledge of the phenomena of adsorption makes it easy to understand that a maximum of the photoemission is eventually reached. As soon as the active spots of the salt surface are all occupied, and the adsorption due to the van der Waals forces begins to dominate, there begin to be formed small, continuous, conducting (see § 16) monatomic layers on the surface, which by means of the absorption of light are able to emit conduction electrons. While all absorption of light by isolated, adsorbed atoms leads to ionization and thus to the emission of electrons,\* this is far from the case with photoemission from metals. We may thus assume that at very small values of  $\theta$  one electron is emitted for every two quanta of light absorbed; at the later (blue) stages this is no longer true. Therefore the photoelectric emission decreases in spite of the naturally increased absorption of light (see also Fig. 77 in § 62).

The maximum in the photoemission curve was formerly ascribed to the formation of the first monatomic adsorbed layer;† but we now understand that it has no connection with such a formation, and that the fraction of the surface covered may be very much smaller than that corresponding to a complete monatomic covering.

If the photoemission is examined with regard to its dependence on the wave-length of the light used, it appears that for various  $\theta$  values belonging to the left-hand part of a curve similar to that in Fig. 83 the threshold is practically constant; for greater values of  $\theta$  belonging to the right-hand part of such a curve the thresholds lie at somewhat shorter wave-lengths. As examples Figs. 84 and 85 give some measurements on a

\* It may be assumed that on the average half of these electrons are emitted toward the outside and the other half into the layer (Chap. xv), since the electrons escape in all directions without any preference.

† J. H. de Boer and M. C. Teves, *Z. Phys.* **65**, 494 (1930).

barium fluoride surface (on silver as a supporting metal) upon which caesium is adsorbed. Curves *a*, *b* and *c* of Fig. 85 are measured in states *a*, *b* and *c* of Fig. 84. The threshold is in this case given by those adsorbed atoms whose ionization limit is most shifted toward longer wave-lengths (see also § 62). Since they are just the atoms which are adsorbed at the most active spots of the surface, these atoms are already present at the smallest values of  $\theta$ , so that the threshold then already has its

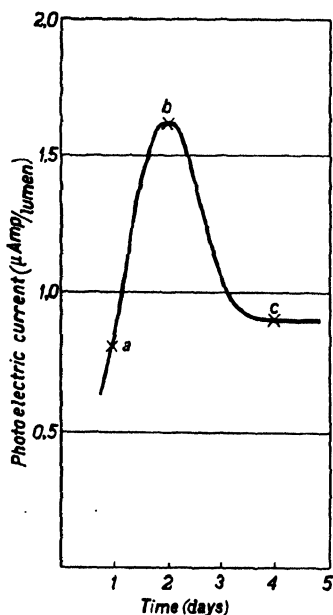


Fig. 84. Variation of photoelectric current with the amount of Cs atoms, adsorbed on a  $\text{BaF}_2$  layer.

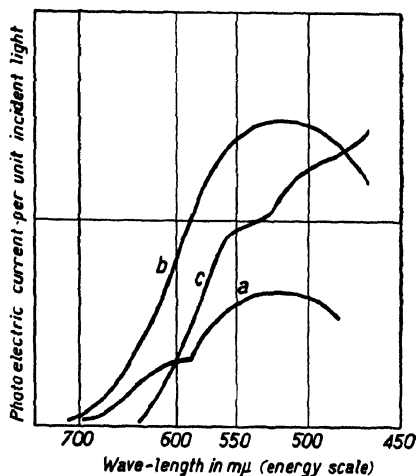


Fig. 85. Spectral distribution curves for Cs on  $\text{BaF}_2$  at the stages *a*, *b* and *c* from Fig. 84. J. H. de Boer and M. C. Teves, *Z. Phys.* 65, 499 (1930).

longest wave-length value. This fact that the threshold is constant at the beginning of the building up of the adsorbed layer is another great difference with the adsorption on metals, where just because of the continual decrease of the work function with increasing  $\theta$  the threshold was shifted gradually toward longer wave-lengths (§ 41).

If in the adsorption on salt layers the value of  $\theta$  is so large that continuous metallic regions occur (to the right of maximum in Figs. 83 and 84; blue colour), then we are concerned

with the threshold of these regions, which lies according to Fig. 85 at somewhat shorter wave-lengths.

As long as we are concerned with separate adsorbed atoms the threshold is given by those atoms which are adsorbed at the most active spots. The position of this threshold depends upon the alkali metal atom adsorbed and upon the type of structure of the adsorbing surface, or rather upon the active spots of that surface. The atoms of other alkali metals give thresholds which lie at somewhat shorter wave-lengths than that given by caesium, since their ionization energies are higher. We have already noted in § 59 that with the salt layers under consideration the outside surface is formed by the negative ions which also determine the active spots. Thus if instead of calcium fluoride, barium fluoride is used, the threshold after the adsorption of caesium lies at about the same place, around  $7000 \text{ \AA.}$ , although the threshold with barium fluoride lies perhaps at slightly longer wave-lengths than with calcium fluoride. In the following sections we shall see that the thresholds may lie at quite different values with other underlayers.

In the action of the photocathodes here described the adsorbed caesium atoms are transformed by the absorption of light into adsorbed caesium ions. As was stated above, in order that a steady photocurrent may be obtained, provision must be made for supplying the emitted electrons. The neutralization of the  $\text{Cs}^+$  ions is brought about by electrons which come from the supporting metal. The problem now is why electrons are drawn out of the supporting metal toward the positive ions. In this connection we must remember that the salt layers used are very thin, and that we are in reality only concerned with the thickness of the separate laminae. If the caesium atom, schematically given in Fig. 86, is transformed into a  $\text{Cs}^+$  ion by photoionization, it is about  $25 \text{ \AA.}$  (see § 59) from the metal surface. Thereby the electric field which the ion causes at the metal surface is very great, and of the order of magnitude of  $2\frac{1}{2} \times 10^6 \text{ volts/cm.}$  This electric field is sufficient to draw an electron out of the metal (§ 9). We thus reach the conclusion\*

\* J. H. de Boer and M. C. Teves, *Z. Phys.* **73**, 198 (1931).



that the supplying of the emitted electrons is brought about through the cold emission of electrons from the metal. It must be remembered that in many electrolysis processes in which ions must be neutralized on the electrodes the same phenomena play a part. The process of neutralization does not take place directly on the electrode in the latter case any more than in the case under consideration.

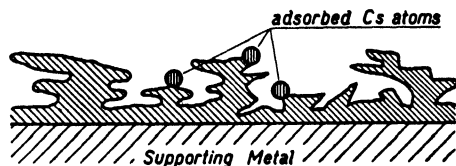


Fig. 86. Diagram for the adsorption of Cs atoms on the active places of a layer of  $\text{CaF}_2$ ,  $\text{BaF}_2$  or a similar layer.

## § 66. The sensitization of potassium by means of hydrogen.

One of the earliest known methods of sensitizing photoelectric cathodes is the treatment of potassium cathodes with hydrogen. Elster and Geitel\* converted the alkali metal into a colourless crystalline hydride which was photoelectrically insensitive to visible light. This hydride was further converted by electron bombardment into a very sensitive, coloured layer. According to a later method, due to the same authors, the same photoelectrically sensitive, coloured layer was reached by a glow discharge in hydrogen. Pohl and Pringsheim† discovered that the layer had acquired a very pronounced selective sensitivity by the glow discharge. We shall not go into the earlier literature on this subject since it has been treated in very great detail in various books about photoelectric phenomena.‡ We shall only review several investigations of recent years.

Very pure potassium has no selective maximum; only after the reaction with hydrogen can a selective maximum be found

\* J. Elster and H. Geitel, *Phys. Z.* **11**, 257, 1082 (1910); **12**, 609 (1911).

† R. W. Pohl and P. Pringsheim, *Verh. dtsh. phys. Ges.* **12**, 682 (1910); **13**, 211 (1911); **15**, 179 (1913).

‡ See, for example: R. Fleischer and H. Teichmann, *Die lichtelektrische Zelle*, pp. 36–9, 69–75, Dresden and Leipzig, Theodor Steinkopff (1932); A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, pp. 165–71 (1932).

at  $436\text{m}\mu$ .\* Molecular hydrogen, when dry, does not react with pure potassium in bulk, so that the photoelectrical sensitivity of pure potassium is not changed by the hydrogen.† If, however, the potassium is in the form of a thin layer on a metal, as platinum, the hydrogen then forms a hydride layer with the potassium‡ and the photoelectric sensitivity falls very sharply (cf. also § 48). The fact that potassium in bulk (thick layer) is not attacked by hydrogen and as a thin adsorbed layer is attacked agrees with the behaviour of caesium which in bulk also cannot be converted into the hydride by hydrogen, but which is easily converted when in the adsorbed state.§

A layer of pure hydride is photoelectrically insensitive. Fleischer and Teichmann evaporated a very thin layer of potassium upon the hydride layer already present, and obtained again a strong photoelectric sensitivity, with the above-mentioned selective maximum at  $436\text{m}\mu$ . The same result was obtained by evaporating potassium in an atmosphere of hydrogen and by the reaction of atomic hydrogen or hydrogen ions|| on potassium.

Elster and Geitel had already explained the characteristic colour of the sensitive alkali metal layer by assuming that colloidal alkali metal was suspended in the otherwise colourless hydride. Gudden and Pohl¶ explain the selective photoelectric effect by assuming that the emitted electrons come from the alkali metal which exists in atomic or molecular solution in the hydride film (or in general according to their conception in the gaseous film\*\*) or which is adsorbed on the film. Gudden and Pohl thus already held the view which is held by the author that adsorbed atoms are the source of the selective photo-

\* G. Wiedmann, *Verh. dtsh. phys. Ges.* **18**, 333 (1916); R. Fleischer, *Ann. Phys., Lpz.*, **82**, 75 (1927).

† O. W. Richardson and A. F. A. Young, *Proc. roy. Soc. A*, **107**, 377, 387 (1925); R. Suhrmann and H. Theissing, *Z. Phys.* **52**, 453 (1928).

‡ R. Fleischer and H. Teichmann, *Z. Phys.* **61**, 227 (1930).

§ J. H. de Boer and C. J. Dippel, *Naturwissenschaften*, **21**, 204 (1933).

|| R. Suhrmann, *Z. Elektrochem.* **37**, 680 (1931).

¶ B. Gudden and R. W. Pohl, *Z. Phys.* **34**, 245 (1925).

\*\* Cf. B. Gudden, *Lichtelektrische Erscheinungen*, p. 109, Berlin, Julius Springer (1928).

electric phenomena. In the absorption of light the valence electrons of the adsorbed atoms are emitted, whereupon as a supplementary process the neutralization of the positive ions formed follows (see also §§ 62, 65 and 71). In all the methods of formation of these selectively active hydride layers we must thus consider that alkali metal atoms are adsorbed on the already formed hydride film. In those methods of formation in which alkali metal atoms are evaporated upon a hydride film, this is immediately evident; in the formation by electron bombardment, glow discharge, ion bombardment, etc. (see above), one may imagine that some potassium is always sputtered, which is then adsorbed on the already formed hydride layer. It is however also possible that the adsorbed layer is formed by surface migration (see below in this same section).

Kluge and Rupp\* studied the structure of these selectively sensitive layers by means of the method of electron reflection. The coloured layers give maxima of deflection for the electron reflection which must be ascribed to potassium, and other maxima which must be ascribed to potassium hydride. Those layers, however, are most selectively sensitive in which the dimensions of the colloidal particles are the smallest, so that it is very probable, and this is also the conclusion of Kluge and Rupp, that the selective photoelectric action must be ascribed mainly to potassium atoms adsorbed as such. This would make this selective emission quite analogous to that which we discussed in the previous section, where on the basis of the absorption spectra we came to the conclusion that the maximum emission occurs when the greatest possible number of atoms are adsorbed in isolated positions, or at least in such a way that there is no noticeable electrical conductivity and thus no question of conduction electrons.

The absorption of light by the adsorbed atoms is thus the cause of the selective emission. Since the absorption depends very much upon the state of polarization of the light, the layers

\* W. Kluge and E. Rupp, *Phys. Z.* **32**, 165 (1931).

must be anisotropic. As we saw in § 64 Fleischer\* found that after the reaction of a small amount of hydrogen with potassium (by heating a hydrogen-charged platinum wire in a cell containing potassium) a selective absorption of light can be measured. The absorption curve for  $\parallel$  light has a maximum at  $436\text{m}\mu$ , that for  $\perp$  light has no such maximum (see Fig. 81 in § 64). In Fig. 87 the photoelectric current per unit incident light is given for  $\parallel$  and  $\perp$  light. If however one plots the photo-

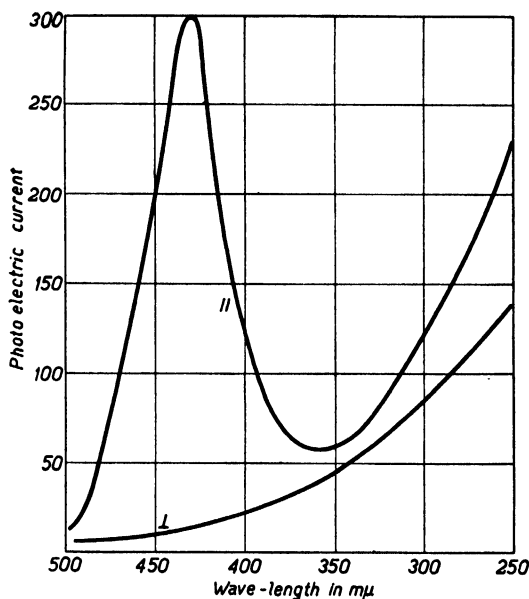


Fig. 87. Hydrogenated potassium. Photoelectric current per unit incident light for  $\parallel$  and  $\perp$  light. Angle of incidence  $45^\circ$ .\*

electric current per unit absorbed light then Fig. 88 is obtained and it is plain that the selectivity is much more clearly exhibited. This may at first glance seem strange since we are seeking to identify the selective property with a selective absorption. We must however remember that in the absorption of light by metals only very few electrons are emitted per number of absorbed light quanta, while in the absorption by the adsorbed atoms in principle every quantum absorbed leads

\* R. Fleischer, *Ann. Phys., Lpz.*, **82**, 75 (1927).

to ionization and half of the electrons liberated in this way are emitted (cf. § 65). Therefore the selectivity in Fig. 88 is so pronounced because in the absorption of light by the atoms the yield of electrons per absorbed quantum is so much better than in the normal photoeffect (thus than in the curve for  $\perp$  light). It may be noted that the absorption curves for pure potassium were also measured by Fleischer, who found a maximum for  $\parallel$  light at  $313\text{m}\mu$ , which was lacking for  $\perp$  light. In agreement with this the curve for the photoelectric current

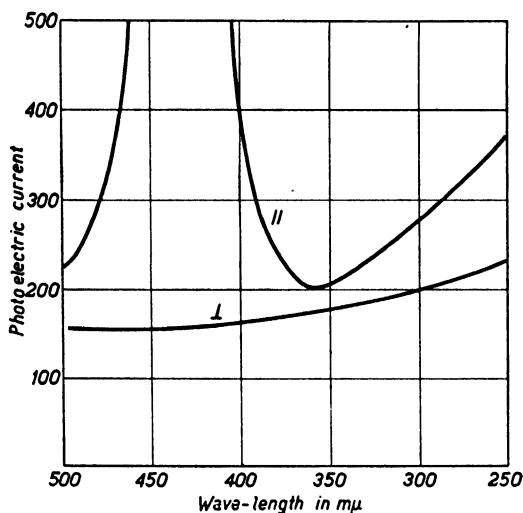


Fig. 88. Hydrogenated potassium. Photoelectric current per unit absorbed light for  $\parallel$  and  $\perp$  light. Angle of incidence  $45^\circ$ . R. Fleischer, *Ann. Phys., Lpz.*, **82**, 75 (1927).

per unit incident light exhibits a maximum at  $313\text{m}\mu$  for  $\parallel$  light, while for  $\perp$  light it does not. In the curve of the current per unit absorbed light, however, this maximum is no longer present. In this case the so-called selective emission must be ascribed only to an increased absorption of  $\parallel$  light and not at the same time to another mechanism of the photoelectric emission. It is characteristic of the selective emission due to the presence of adsorbed atoms that the process is controlled by quite a different mechanism of electron emission (photoionization) to that in the case of the normal photoeffect (emission of conduction electrons).

Lukirsky and Rijanoff\* let known amounts of atomic hydrogen react with potassium and examined the photoelectric current as to its dependence on the amount of hydrogen taken up. The atomic hydrogen was made by heating a tungsten filament in hydrogen at low pressure. Curve *a* in Fig. 89 represents the amount of hydrogen taken up as a function of the time during which the tungsten filament was heated. It can be seen that the amount taken up increases at first linearly with the time, then increases more slowly, and finally becomes constant. Curve *b* gives the photoelectric current which also rises at first linearly with the time, reaches a maximum when just half of the final total amount of hydrogen is taken up, and then falls again to a value lower than that of pure potassium, where it remains constant when no more hydrogen is being taken up. If the experiment, instead of being carried out at room temperature, is carried out at  $-180^{\circ}\text{C.}$ , only half as much hydrogen is taken up and the photoelectric current does not rise, but falls directly to a somewhat lower value. If the hydrogen is afterwards pumped off and the temperature raised to room temperature, the photoelectric current suddenly rises to a value corresponding to the maximum of curve *b* in Fig. 89. More hydrogen can now be taken up to an amount equal to that which is already present, so that the final amount is just the same as was taken up at room temperature. The photoelectric current falls during this second taking up of hydrogen according to a curve which corresponds to the right branch of curve *b* in Fig. 89. An explanation which may be given for this behaviour is the following. A monomolecular hydride film is formed on the potassium surface by means of the atomic hydrogen. A monatomic layer of potassium is adsorbed on this hydride layer; every area of hydride formed is immediately covered with potassium by the rapid surface migration at room temperature. Consequently the photoelectric current rises in direct proportion to the number of atoms adsorbed (see also § 65) and thus with the time. This continues until the whole potassium surface is covered with a monomolecular hydride

\* S. Rijanoff, *Z. Phys.* **71**, 325 (1931); P. I. Lukirsky and S. Rijanoff, *Z. Phys.* **75**, 249 (1932); P. I. Lukirsky, *Phys. Z. Sowjet.* **4**, 225 (1933).

film and this in turn with a monatomic layer of potassium. This adsorbed potassium layer can now also take up hydrogen to an amount just equal to that already taken up, but this makes the photocurrent fall since an adsorbed layer of potassium can no longer be formed on this new hydride surface. At  $-180^{\circ}\text{C}$ . surface migration is entirely lacking; the hydride layer formed is thus not covered with adsorbed potassium, the strong selective photoeffect does not appear, and only half as much hydrogen has been taken up as at room temperature. If the

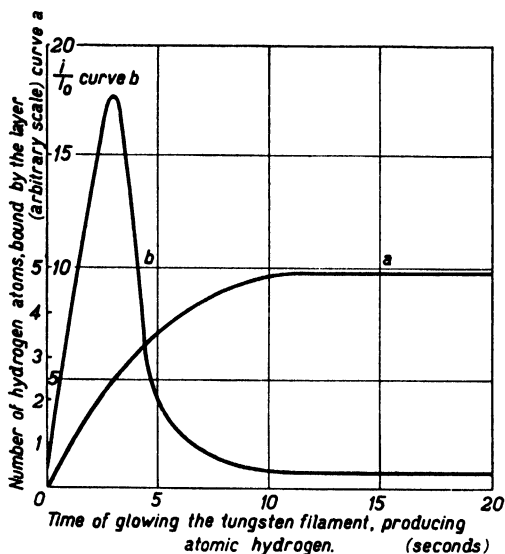


Fig. 89. Amount of hydrogen, taken up by potassium (curve *a*) and photoelectric current of this layer (curve *b*) as a function of the time of glowing a tungsten filament, producing atomic hydrogen. According to Lukirsky and Rijnoff.

system is then warmed to room temperature, an adsorbed layer of potassium is formed because of its recovered mobility, and at the same time the selective photoeffect is obtained. Hydrogen can now again be taken up whereby the selective photoeffect disappears. Thus the final state at  $-180^{\circ}\text{C}$ . can be represented schematically by the symbol  $[\text{K}]\text{-KH}$ , and that at room temperature by  $[\text{K}]\text{-KH-KH}$ .

Experiments at  $-63^{\circ}\text{C}$ . show that at this temperature the surface migration is still sufficiently strong to keep up with the addition of hydrogen and the phenomena are similar to

those at room temperature. At  $-112^{\circ}\text{C}$ ., however, the surface migration goes very much slower than the taking up of hydrogen, although its velocity is not yet reduced to practically zero.

A layer, which in Lukirsky and Rijanoff's experiments has taken up as much hydrogen as it can, may again be made selectively sensitive by evaporating more potassium upon it. Such a layer may be represented by the symbol



Lukirsky and Rijanoff have prepared still more complicated layers.

### § 67. The reaction of oxygen on potassium.

Not only by the reaction of hydrogen but also by the reaction of oxygen on alkali metals can a selective photoelectric effect be obtained. Pohl and Pringsheim\* let dry oxygen react on potassium. At very low pressures no reaction was obtained, at somewhat higher pressures (a few tenths of a millimetre) a reaction was obtained in which the potassium became covered with a coloured layer (green-blue to deep black). The photoelectric sensitivity had thereby risen sharply and a selective emission with a maximum at  $405\text{ m}\mu$  was obtained. By analogy with the structure of the coloured hydride films, discussed in § 66 (obtained by a glow discharge in hydrogen), we may here, with Pohl and Pringsheim, assume that potassium is colloiddally dispersed in a layer of some potassium-oxygen compound. On the basis of what we saw in §§ 65 and 66 the selective emission is to be understood as a photoionization of potassium atoms which are adsorbed on potassium oxide (probably  $\text{K}_2\text{O}$ ), and we may therefore indicate these cathodes by the symbol  $[\text{K}]\text{-K}_2\text{O-K}$ . By this symbol we mean that upon solid potassium (indicated by square brackets) there is a layer of  $\text{K}_2\text{O}$  upon which potassium atoms are adsorbed.

The activation of potassium by oxygen was investigated later by Wiedmann† and by Fleischer,‡ both of whom found

\* R. W. Pohl and P. Pringsheim, *Verh. dtsh. phys. Ges.* **15**, 625 (1913).

† G. Wiedmann, *Verh. dtsh. phys. Ges.* **18**, 333 (1916); *J. Radioakt.* **19**, 135 (1922).

‡ R. Fleischer, *Ann. Phys.*, Lpz., **82**, 243 (1927).



a selective maximum not at  $405\text{m}\mu$  but at  $313\text{m}\mu$ . It occurs to us that cause of this difference with Pohl and Pringsheim must be sought in the construction of the cathode. Fleischer first allowed oxygen to react on potassium and obtained a black coating which was inactive photoelectrically. Then the system was heated to the melting point of potassium and kept at that temperature until the surface was again quite colourless and had regained a completely metallic lustre. Under these conditions the selective maximum is measured and found at  $313\text{m}\mu$ . One may no longer assume that there is a layer of  $\text{K}_2\text{O}$  on the potassium in this case, but may assume a covering with a few adsorbed oxygen ions, which as we have seen in §§ 46 and 47 may remain stable on the surface under conditions which would cause the normal oxide to dissociate or disappear. In addition to these oxygen ions on the surface we may assume the adsorption of potassium ions and of potassium atoms next to the ions, potassium ions and atoms which are not yet in the lattice relation with the underlying potassium metal. Considering it in this way we must compare this case with the adsorption of oxygen ions on tungsten or silver, where caesium ions and caesium atoms were adsorbed next to the oxygen atoms as treated in § 50. In other words we would like here to compare the potassium surface treated with oxygen, which Fleischer investigated, with the  $[\text{W}]\text{-O,Cs}$  and  $[\text{Ag}]\text{-O,Cs}$  cathodes discussed in § 50, and we may therefore indicate the cathodes now under discussion by the symbol  $[\text{K}]\text{-O,K}$ . As was stated in § 50 such cathodes exhibit, beside the normal photoeffect (at sufficiently long wave-length) which is strengthened by the help of the double layer, also a selective photoeffect at sufficiently short wave-length. One must indeed, as we shall see more clearly in § 71, always expect a selective photoeffect when one is concerned with adsorbed atoms. The photoionization of the adsorbed atoms—on metal surfaces as well as on the surfaces of chemical compounds—is the cause of the selective photoeffect. In general the bands of the absorption spectra and thus the regions of the selective photoemission lie farther toward the ultraviolet in the adsorption of atoms on metal surfaces than in their adsorption on halide,

hydride or oxide surfaces (see also § 70), so that on these grounds also the position of the selective maxima of the [K]-K<sub>2</sub>O-K cathode discussed above at 405 m $\mu$  and of the [K]-O,K cathode at 313 m $\mu$  becomes clear.

When a [K]-K<sub>2</sub>O-K cathode is made by oxidizing potassium with gaseous oxygen, the sensitivity rises with the amount of oxide formed until a maximum is reached. When still more oxygen is taken up, the sensitivity falls as the oxide layer forms a greater and greater hindrance for the passage of the electrons (cf. also § 92). According to Timofeew and Nalimow\* the maximum is reached when  $40 \times 10^{-5}$  gram of oxygen per cm.<sup>2</sup> potassium is taken up.

In the work of Fleischer referred to above, as well as in the work on the sensitization by hydrogen referred to in § 66, the photoemission as well as the absorption of light was measured as a function of wave-length for  $\parallel$  and for  $\perp$  light, whereby it again appeared that, measured per unit of absorbed light, the selective effect for  $\parallel$  light continued to be present. The explanation is here the same as in the case of the hydrogenated layers, viz. that in the absorption of light by adsorbed atoms every quantum absorbed leads to the emission of one electron, while this is not the case in the emission of conduction electrons from the underlying metal.

As was stated in § 66 pure potassium shows no selective photoeffect when the photoemission is measured per unit of absorbed light. The maximum found in the measurements per unit of incident light must be ascribed to an increased absorption of light, but it is not the result of a different mechanism of emission. This latter maximum gradually shifts toward shorter wave-lengths, as the potassium becomes more thoroughly outgassed. Fleischer† succeeded in driving the maximum back to 402 m $\mu$ . Perhaps completely outgassed potassium would show no maximum at all. In the case of a lithium surface, freshly cut *in vacuo*, no selective photoeffect is found; after the surface has been kept for some time the photoemission rises and a maxi-

\* P. W. Timofeew and W. W. Nalimow, *Z. Phys.* **81**, 687 (1933).

† R. Fleischer, *Ann. Phys., Lpz.*, **82**, 249 (1927).

mum is produced at about  $300\text{m}\mu$ , due to the taking up of gases.\*

### § 68. Caesium-oxygen cathodes and caesium-caesium oxide cathodes.

If we compare the reaction of oxygen on caesium with that of oxygen on potassium it is striking that large amounts of oxygen can be taken up by caesium with no change of photoelectric sensitivity,† while with potassium a surface oxidation has a sensitizing action. The cause of this difference must be sought in the difference of mobility and rate of surface migration of the two alkali metals. In the case of potassium, upon relatively rapid oxidation (Fleischer, § 67) an oxide film is formed upon which no potassium atoms are adsorbed, so that a sharp lowering of the photoelectric sensitivity is the result (negative oxygen ions on the outside); upon careful and relatively slow oxidation (Pohl and Pringsheim, § 67) a layer of  $\text{K}_2\text{O}$  is formed upon which, due to the surface migration, potassium atoms are adsorbed and cause the selective sensitivity at  $405\text{m}\mu$  which was mentioned in § 67. Koller† allowed oxygen to react quite slowly at room temperature on caesium. In this process a polyatomic layer of adsorbed caesium is immediately formed on the oxide already present, or as we may perhaps also express it, the caesium oxide formed is dissolved in the caesium (absorbed by it). The result is that the surface is practically unchanged, and therefore the photoelectric sensitivity also remains the same. Only after the caesium is almost completely oxidized does a very thin adsorbed caesium layer appear on the caesium oxide. Upon still further oxidation a monatomic layer of caesium and finally only individual adsorbed caesium atoms are left. In these later stages the photoelectric sensitivity must be much greater, and is found experimentally to be so. When the caesium is almost completely oxidized the photocurrent suddenly rises. When the supply of oxygen is continued the photocurrent immediately falls to

\* R. A. Millikan and W. H. Sonder, *Proc. Nat. Acad. Sci.*, Wash., 2, 19 (1916).

† L. R. Koller, *Phys. Rev.* 36, 1643 (1930).

zero, since the adsorbed caesium is now also oxidized. Instead of carrying out his experiment at room temperature Koller also carried it out at a very low temperature ( $-180^{\circ}\text{C}.$ ). In this case the photoelectric sensitivity rose immediately after the first addition of oxygen, so that it must be assumed that at this temperature the surface migration of caesium provides approximately only a monatomic adsorption of caesium atoms on the caesium oxide already formed. Continued supply of oxygen causes the oxidation of the adsorbed caesium and the photoelectric sensitivity falls again to zero. The mass of

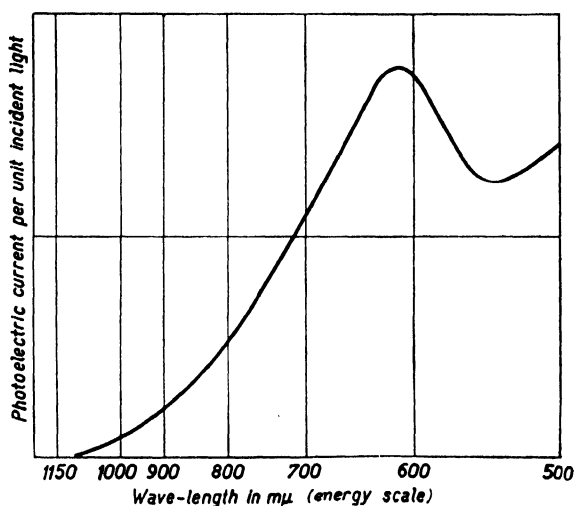


Fig. 90. Spectral distribution curve for a  $[\text{Ag}]\text{-Cs}_2\text{O-Cs}$  cathode.

caesium under this surface oxide film is not further oxidized at this temperature; it is protected against further attack.

Due to this accidental condition it is only possible to make a  $[\text{Cs}]\text{-Cs}_2\text{O-Cs}$  cathode at a low temperature; however if one substitutes for caesium another less mobile metal one can naturally make a cathode stable at room temperature,  $[\text{Me}]\text{-Cs}_2\text{O-Cs}$ . If one first deposits a relatively thin layer of caesium on silver, oxidizes this layer, and afterwards admits more caesium, one obtains a  $[\text{Ag}]\text{-Cs}_2\text{O-Cs}$  cathode.\* The spectral sensitivity of such a  $[\text{Ag}]\text{-Cs}_2\text{O-Cs}$  cathode is represented in Fig. 90, from which it may be seen that the caesium

\* J. H. de Boer and M. C. Teves, *Z. Phys.* **65**, 500 (1930).

atoms adsorbed on caesium oxide call into existence a selective photoeffect with a maximum at  $607\text{ m}\mu$ . If the cathode is prepared by some other method, for example by first letting oxygen be adsorbed on silver at room temperature, then pumping off the excess of oxygen at room temperature, and then still at room temperature allowing caesium to react upon the adsorbed oxygen layer, a monomolecular layer of  $\text{Cs}_2\text{O}$  is obtained on the silver, upon which layer caesium atoms are adsorbed. The spectral sensitivity of this cathode is represented in Fig. 91. The maximum is at practically the same place as

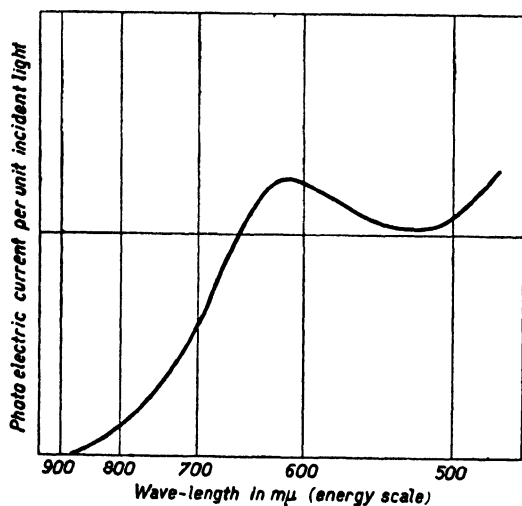


Fig. 91. Spectral distribution curve for a [Ag]- $\text{Cs}_2\text{O}$ -Cs cathode with a monomolecular layer of  $\text{Cs}_2\text{O}$ .

when the  $\text{Cs}_2\text{O}$  layer is thicker. The only difference is that the photoelectric threshold in the case of the thick intermediate layer is somewhat farther toward long wave-lengths, probably due to the fact that with a thicker layer of  $\text{Cs}_2\text{O}$  as adsorbent there are more and stronger active spots on the surface.

The [Ag]- $\text{Cs}_2\text{O}$ -Cs cathode just described with a monomolecular layer of  $\text{Cs}_2\text{O}$  is, with regard to its structure and its properties, quite different from the [Ag]-O,Cs cathode described in §§ 50 and 67. In the preparation of the [Ag]-O,Cs cathode, according to Bainbridge and Charlton\* the silver was

\* Cf. L. R. Koller, *J. opt. Soc. Amer.* **19**, 141, 143 (1929); *Phys. Rev.* **36**, 1639 (1930).

charged with oxygen in a different way, and then with caesium, not at room temperature but at  $300^{\circ}\text{C}$ . At such a temperature no  $\text{Cs}_2\text{O}$  can be formed and one obtains an adsorption of oxygen ions and caesium ions and atoms next to each other on the surface of the silver. The spectral sensitivity is then also quite different, as can be seen from Fig. 92.

One can also prepare photoelectric cathodes on metal surfaces such as silver, which exhibit a selective maximum lying farther toward long wave-lengths than that of the above-mentioned  $[\text{Ag}]-\text{Cs}_2\text{O}-\text{Cs}$  cathodes, but since in these cases the

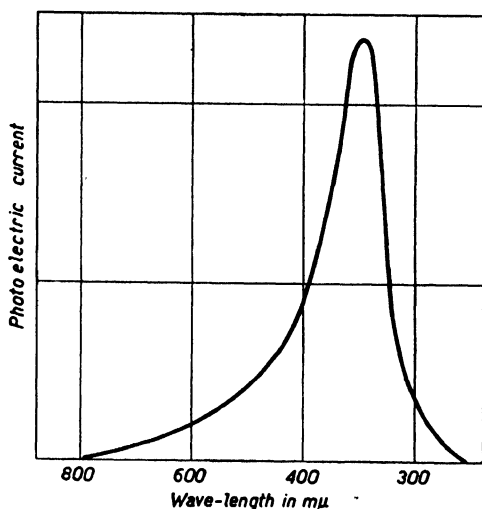


Fig. 92. Spectral distribution curve for a  $[\text{Ag}]-\text{O,Cs}$  cathode.  
L. R. Koller, *Phys. Rev.* **36**, 1640 (1930).

intermediate layer consists not only of  $\text{Cs}_2\text{O}$  but also of metal particles such as silver for example and in many cases of caesium particles too, they will be discussed later (§§ 94 and 95).

### § 69. Other cases of sensitization of the alkali metals by chemical compounds.

The reaction of oxygen upon sodium also raises the photoelectric effect of this metal, especially for the longer wave-lengths.\*

\* P. Selényi, *Phys. Z.* **30**, 933 (1929); *Photoelectric Cells and their Applications*, edited by J. S. Anderson, Phys. and Opt. Societies, London (1930), p. 25; A. R. Olpin, *Phys. Rev.* **36**, 260 (1930).

The threshold is shifted to about  $800\text{ m}\mu$ , while there is an indication of a maximum at about  $500\text{ m}\mu$ .

A selective photoeffect can also be obtained with the help of sulphur, selenium or tellurium instead of oxygen. Kluge\* let these elements react upon potassium in such a way that the structure of the surfaces can be compared with the  $[\text{K}]\text{-K}_2\text{O-K}$  cathode described by Pohl and Pringsheim (§ 67). The position of the selective maxima found is as follows:

$[\text{K}]\text{-K}_2\text{O-K}$	at $405\text{ m}\mu$ ,
$[\text{K}]\text{-K}_2\text{S-K}$	at $410\text{ m}\mu$ ,
$[\text{K}]\text{-K}_2\text{Se-K}$	at $425\text{ m}\mu$ ,
$[\text{K}]\text{-K}_2\text{Te-K}$	at $430\text{ m}\mu$ .

Olpin† obtained a maximum at  $410\text{ m}\mu$  with a  $[\text{K}]\text{-K}_2\text{S-K}$  cathode while a  $[\text{Na}]\text{-Na}_2\text{S-Na}$  cathode showed a maximum at  $360\text{ m}\mu$ , but remarkably enough just as in the case of sensitization by oxygen it had a threshold shifted much farther toward long wave-lengths than the corresponding potassium cathode, and in addition it also showed an indication of a maximum at  $500\text{ m}\mu$ .

Fleischer and Teichmann‡ studied the influence of  $\text{NO}$ ,  $\text{NO}_2$  and nitrogen on the photoelectric sensitivity of potassium, and found strong selective maxima at  $334\text{ m}\mu$  ( $\text{NO}$ ) and especially at  $365\text{ m}\mu$  ( $\text{NO}_2$ ).

Further the influence of halogens, halogen acids, hydrogen sulphide, sulphur dioxide, carbon dioxide, etc. has been investigated.§

We shall see later (§ 74) that by irradiation of the alkali halides with short wave light within their own absorption bands alkali atoms are produced. These alkali metal atoms give rise to an internal photoelectric effect (photoelectric conduction). In the case of thin layers of alkali halide, however, some alkali metal atoms always reach the outer surface. Fleischmann|| discovered that in such a case the salt layer also

\* W. Kluge, *Z. Phys.* **67**, 497 (1931).

† A. R. Olpin, *Phys. Rev.* **36**, 258 (1930).

‡ R. Fleischer and H. Teichmann, *Z. Phys.* **60**, 317 (1930); **67**, 184 (1931).

§ For bibliography see R. Fleischer and H. Teichmann, *Die lichtelektrische Zelle*, pp. 40–6 (1932).

|| R. Fleischmann, *Z. Phys.* **84**, 717 (1933).

exhibits an external photoelectric emission, which is also, according to this experiment, proportional to the number of alkali metal atoms formed.

Sensitization by two or more independently reacting elements or compounds at the same time has also repeatedly been described. As examples we may mention the sensitization of potassium by oxygen and hydrogen together,\* or the sensitization by oxygen and sulphur together.†

Olpin‡ allowed various organic substances to react on potassium or sodium, for example: benzene, carbon disulphide, acetone and nitrobenzene, and also many organic dyes such as are used for sensitizers in photography. The selective maximum in the case of sodium was shifted most toward long wave-lengths by cryptocyanine ( $\sim 550\text{m}\mu$ ).

Suhrmann§ evaporated upon compact potassium first a very thin layer of naphthalene and then upon this thin film of naphthalene a small amount of potassium. The potassium adsorbed on the naphthalene film causes a strong selective maximum of the photoelectric sensitivity at  $420\text{m}\mu$ . This cathode may thus be indicated by the symbol  $[\text{K}]\text{-C}_{10}\text{H}_8\text{-K}$ . If instead of naphthalene paraffin was chosen, Suhrmann obtained no selective photoeffect. This result agrees completely with the fact that potassium is either not at all or very slightly adsorbed by paraffin.||

Finally it must be mentioned that spontaneously adsorbed layers of rubidium on glass show a very pronounced selective photoeffect. Ives and Johnsrud¶ showed that these layers are at the most one atom thick, and that here again it is especially

\* O. W. Richardson and A. F. A. Young, *Proc. roy. Soc. A*, **107**, 386 (1925); N. R. Campbell, *Phil. Mag.* **6**, 633 (1928); R. Fleischer, *Ann. Phys.*, Lpz., **82**, 243 (1927).

† A. R. Olpin, *Phys. Rev.* **36**, 251 (1930).

‡ A. R. Olpin, *Phys. Rev.* **36**, 265 (1930).

§ R. Suhrmann, *Z. Elektrochem.* **37**, 678 (1931); *Phys. Z.* **32**, 929 (1931); *Z. wiss. Photogr.* **30**, 161 (1931).

|| J. H. de Boer and M. C. Teves, *Z. Phys.* **73**, 192 (1931).

¶ H. E. Ives and A. L. Johnsrud, *Astrophys. J.* **62**, 309 (1925); *J. opt. Soc. Amer.* **15**, 374 (1927).



|| light which gives the high selective photoemission. It was mentioned in § 64 that Fleischmann showed that || light was absorbed selectively by similar layers of potassium on glass.

### § 70. The selective photoeffect in the adsorption of alkali metal atoms on metal surfaces.

In the adsorption of alkali metal atoms and also of alkaline earth metal atoms on surfaces of various chemical compounds such as fluorides (§ 65), hydrides (§ 66), oxides (§§ 67 and 68), etc., and even of organic compounds (§ 69), we obtain as we have seen in the previous sections selective photoelectrically active surfaces. The photoelectrons in these cases originate in the adsorbed atoms themselves. As has already been stated several times and as will be discussed in more detail in § 71 we are here concerned with a photoionization of these adsorbed atoms.

In the adsorption of alkali metal atoms on metal surfaces we may also expect such a photoionization, and consequently the selective photoeffect. We already know from the treatment of thermionic emission in Chaps. III and IV, that at small values of  $\theta$  no alkali or alkaline earth metal atoms but only alkali or alkaline earth metal ions are adsorbed. Only at greater values of  $\theta$  (with caesium on tungsten from  $\theta$  = about 0.134) are the atoms no longer transformed into ions on the surface but adsorbed as such. Only then may we expect the presence of the selective photoeffect, and we have seen in the various sections of Chap. V that this is in complete agreement with the experimental facts. Thus it was stated in § 43, that a co-operation of the adsorbed atoms in raising the photoemission is not appreciable when the work function of the surface is lowered by less than 0.4 of the maximum possible lowering, but that thereafter the adsorbed atoms may be counted on to contribute to the photoeffect. It now appears that the selective photoeffect, at those fractions of surface covered at which it first begins to be appreciable, lies at very short wave-lengths, and that selective maxima are found at longer wave-lengths only upon increased values of  $\theta$  (see also § 42). Thus we have already seen in § 44 that the measurements of Suhrmann and Theis-

sing\* of the dependence on temperature of the photoemission of platinum covered with a small amount of sodium, indicate that there is a selective maximum, for the small values of  $\theta$  used, at wave-lengths shorter than  $240\text{m}\mu$  (Fig. 55 in § 44). At greater values of  $\theta$  a selective maximum is found at about  $315\text{m}\mu$ . This behaviour shows that at those values of  $\theta$  at which the selective effect first becomes appreciable and lies at very short wave-lengths, the photoionization of the adsorbed sodium atoms requires as much or perhaps even more energy than the photoionization of free sodium atoms. According to the value of the ionization potential, 5.12 volts, free sodium atoms are ionized by light of a wave-length of  $240\text{m}\mu$ .

The position of the selective photoemission band at such short wave-lengths may be expected when we examine the potential curves for the case. Let us take as example the adsorption of caesium on tungsten and examine the potential curves at the moment when the adsorption in the form of ions passes over into an adsorption of atoms ( $\theta = 0.134$ ). As we have seen in the discussion of Fig. 36 in § 28 the adsorption energy for adsorption in the form of positive ions at this moment has risen to  $Q_i = 3.15$  electron volts and the adsorption energy of the caesium atoms added next to the ions is 2.55 electron volts. These atoms are now ionized in the selective photoeffect, and in order to ascertain how much energy is required to do this we must ascertain the vertical distance from point  $B'$  of the curve  $AB'C'$  in Fig. 93, which corresponds to Fig. 36 in § 28, to an ionic potential curve  $def$  which is drawn parallel to  $D'E'F'$  and in which the level  $d$  lies 3.88 volts above the level  $A$  of curve  $AB'C'$ . If the valence electron of the caesium atom should be taken up in the metal, we would pass from curve  $AB'C'$  to curve  $D'E'F'$ , in which  $D'$  lies higher than  $A$  by an amount  $I - \epsilon\phi_\theta$ . If however the electron is emitted, we pass to curve  $def$ , in which  $d$  is higher than  $A$  by an amount  $I$  as in Fig. 78 of § 62. Although we really do not know the exact form of curve  $def$ , we can still see that the distance  $B'g$  is of the same order of magnitude or even greater than the

\* R. Suhrmann and H. Theissing, *Z. Phys.* **73**, 709 (1932).

distance  $Ad$ , in other words, that in this case the absorption of light which leads to ionization must be expected to lie at shorter wave-lengths than if we were concerned with free atoms. This expectation is strengthened by the fact that curve  $lef$  is very probably drawn with too strong a minimum (too great adsorption energy for the ion). In the ionization of an atom adsorbed next to a positive ion, a positive ion is formed next to one already present, so that the combining energy of

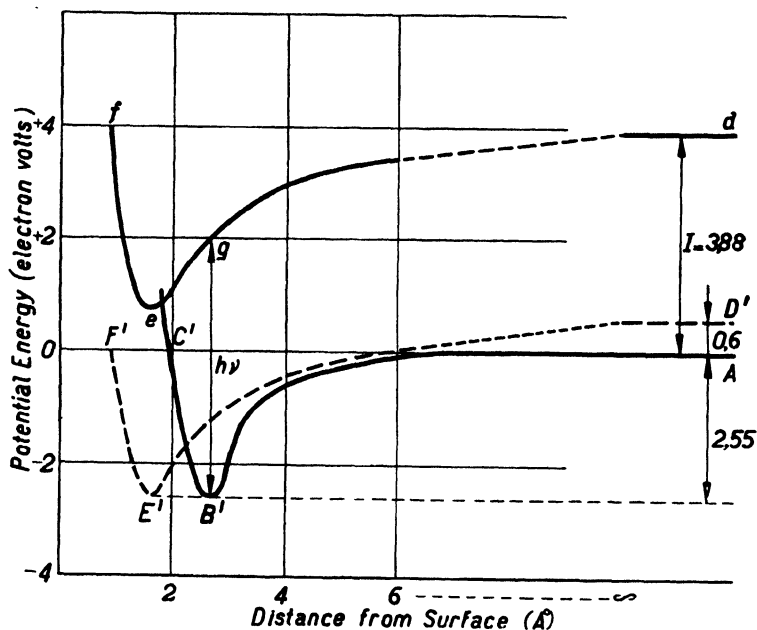


Fig. 93. Potential curves for the selective photoelectric effect of caesium atoms, adsorbed on a metal surface, next to caesium ions.

this new ion is much smaller than that of a free ion on the metal surface.

If now at greater values of  $\theta$  we have reached the moment when no more new atoms are adsorbed next to positive ions, but between atoms already present, we may expect the selective photoeffect at very much longer wave-lengths. The adsorption energy of the atoms which are no longer adsorbed next to ions is much lower, so that we do not begin at the minimum  $B'$  of curve  $AB'C'$  but from the minimum  $B''$  of curve  $AB''C''$  (Fig. 94). In addition the potential curve of the

ion now formed is not higher but even lower than *def*, since in this case the ion is formed not only not next to a positive ion, but even between atoms, so that its combining energy is considerably greater. Instead of having a transition from *B'* to *g*, we have one from *B''* to *g'*, and we may expect an absorption of light and thus a selective photoelectric emission at longer wave-lengths. Thus because the adsorption energy for the atoms decreases and that for the ions increases (cf. also § 28) the selective photoeffect is shifted toward longer wave-lengths with increasing  $\theta$ . Especially at the moment when the atoms

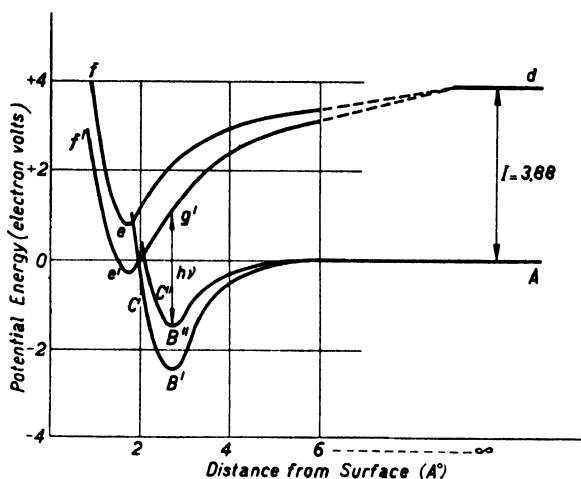


Fig. 94. Potential curves for the selective photoelectric effect of caesium atoms, adsorbed on a metal surface, next to other caesium atoms.

are no longer adsorbed next to ions, but between other atoms, at which moment the minimum of the work function is also reached, may the selective photoeffect be expected at longer wave-lengths. Under these conditions the ionization of the adsorbed atom will also proceed more easily than that of the free atom, so that the selective photoelectric maximum will lie at longer wave-lengths than the ionization limit of the free atom.

We have already seen above how it seems to follow from the measurements of Suhrmann and Theissing that for sodium on platinum the behaviour is actually such as would be expected on the basis of the picture here drawn.

All the examples mentioned in Chap. v are in agreement with this picture. We may especially mention the research of Suhrmann and Theissing\* on the photoeffect in the adsorption of potassium on platinum. When only a small amount of potassium is adsorbed on the platinum mirror, a normal sensitivity curve is measured also for  $\parallel$  light. Whether at a certain moment at very short wave-lengths a selective effect could be measured, cannot be determined on the basis of these measurements. The vector relation, that is to say the relation between the sensitivity for  $\parallel$  light and for  $\perp$  light, is normal in the spectral range examined, and is entirely due to the optical properties of the platinum. At the moment when the photoelectric threshold has reached its greatest excursion and afterwards with increasing  $\theta$  is retreating again toward shorter wave-lengths (atoms next to atoms which are next to ions) a selective effect is measured at  $340\text{ m}\mu$ , that is at a wave-length which is longer than the ionization limit of free potassium ( $283\text{ m}\mu$ ). If more potassium is adsorbed, the maximum appears at first to remain about constant (as does the threshold after it has retreated somewhat from its maximum excursion), in order afterwards when just visible potassium layers are formed to be shifted to  $400\text{ m}\mu$  when more atoms are added than correspond to the monatomic layer.

Not only in the adsorption of alkali or alkaline earth metal atoms on the surface of metals like tungsten, platinum or silver is a selective photoelectric effect found, but also in the adsorption of caesium on magnesium,† in which case also the selective maximum lies farther toward long wave-lengths than the ionization limit of caesium. The much studied selective photoemission of the alloys of the alkali metals with each other, of sodium-potassium alloys for example, may perhaps also be classified with these phenomena. It is quite reasonable to suppose that in a sodium-potassium alloy especially the atoms of the more mobile alkali metal, potassium in this case, should be adsorbed on the surface.

In the [K]-O,K and [Ag]-O,Cs cathodes discussed in §§ 67

\* R. Suhrmann and H. Theissing, *Z. Phys.* **55**, 701 (1929).

† V. Zworykin and E. D. Wilson, *J. opt. Soc. Amer.* **19**, 81 (1929).

and 68 we are also concerned with the selective photoemission of alkali metal atoms which are adsorbed on metal surfaces, in this case next to positive alkali metal ions and negative oxygen ions.

### § 71. The cause of the selective photoeffect.

As has been repeatedly stated (Chaps. v, VIII, §§ 62 and 64, and the previous sections of this chapter) according to our view the selective photoemission must be regarded as a photo-ionization. In principle this standpoint was already adopted by Pohl\* when he assumed the presence of finely dispersed alkali metal whose absorption of light led to the emission of electrons, in order to explain the selective photoeffect of cathodes similar to those which we here indicate by the symbols [K]-KH-K or [K]-K<sub>2</sub>O-K. Also in the case of adsorption directly on metals the presence of adsorbed atoms leads to the possibility of photoionization and thus of selective photoemission. In this process, as has already been explained sufficiently, one must not imagine a liberation of the electrons by a secondary action of the atoms excited by the absorption of light, as is the case in the giving up of electrons in caesium vapour at the absorption lines (§ 56), but an ionization which occurs immediately during the primary process of absorption of light and in which the Franck-Condon principle must be applied.†

On the basis of their experiments Campbell‡ as well as Suhrmann§ came to the conclusion that for the occurrence of a selective photoelectric effect it was necessary that the alkali metal be separated from the supporting metal by some kind of intermediate layer which serves as binder.

Campbell concluded that an electronegative element must be present as binding material, and considers the distinctive course of the potential given by such an arrangement of first

\* R. W. Pohl, *Naturwissenschaften*, **14**, 214 (1926).

† J. H. de Boer, *Chem. Weekblad*, **29**, 34 (1932); J. H. de Boer and M. C. Teves, *Z. Phys.* **83**, 521 (1933).

‡ N. R. Campbell, *Photoelectric Cells and their Applications*, p. 10, Phys. and Opt. Soc., London (1930).

§ R. Suhrmann, *Phys. Z.* **32**, 216 (1931); *Z. wiss. Photogr.* **30**, 161 (1931).

an electronegative layer and then an electropositive layer on the surface to be the source of the selective emission. In agreement with Fowler\* the selective photoeffect is considered as a selective transmission of the conduction electrons through the intermediate layer. In this conception it is thus assumed that it is the conduction electrons of the supporting metal which are emitted. Fowler deduced on the basis of wave mechanics that when in front of a surface there is first a potential hill, then a potential valley, and then again a potential hill (Fig. 95), an electron with the energy  $W$  is prefer-

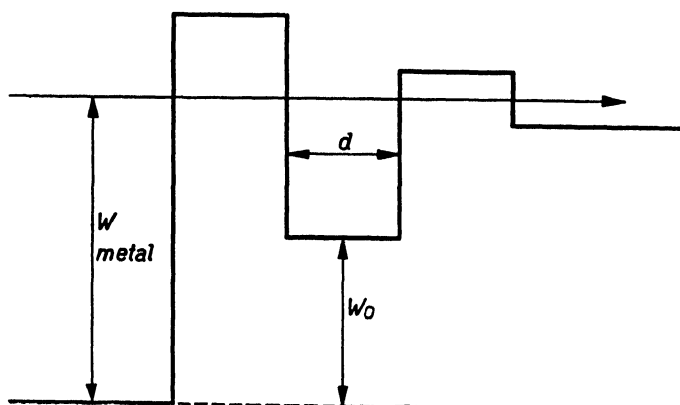


Fig. 95. Potential barrier, assumed by Fowler, showing a selective electron transmission.

entially allowed to pass through these surface layers, when the difference in energy  $W - W_0$ —thus the surplus energy which the electron has above the minimum of the potential valley ( $W_0$ , see Fig. 95)—has a definite relation to the width of the valley  $d$ . This relation

$$W - W_0 = n^2 \frac{h^2}{8md^2},$$

in which  $n$  is an integer,  $h$  Planck's constant (§ 2) and  $m$  the mass of the electron, is such that the de Broglie wave-length (§ 8) of the electron forms standing waves in the valley.

Olpin† attempted to test this relation quantitatively, assuming that all energy possessed by the emitted electron above

\* R. H. Fowler, *Proc. roy. Soc. A*, **128**, 123 (1930).

† A. R. Olpin, *Phys. Rev.* **38**, 1745 (1931).

the level  $W_0$  is taken up as a whole from the absorbed light quantum, thus that

$$W - W_0 = h\nu.$$

In that case the following relation holds for the frequency of the maximum of the selective photoeffect

$$\nu = \frac{h}{8\pi d^2},$$

where  $n$  has already been set equal to 1. Olpin found a very good agreement with the experimentally found selective maxima, when for  $d$  he set definite distances at which the ions stand in the lattices of the hydrides or oxides of the intermediate layers. Olpin calculated these distances in many cases from the ion radii. Zachariasen\* noted that when one substitutes in the formula the distances known from X-ray analysis, the agreement between the measured and the calculated value of  $\nu$  (value of  $\lambda$ ) is much less satisfactory. In addition Olpin's assumption that  $W - W_0 = h\nu$  is very arbitrary, since the value of  $h\nu$  measured in the emission of conduction electrons from a metal is equal to  $W - W_i$  (see §§ 3 and 5) and it would be quite accidental if  $W_0$  and  $W_i$  were at the same level.

According to Frenkel† Fowler's idea of ascribing the selective photoemission to a selective transmission is correct, but his conception of the course of the potential is too complicated.

We shall not go deeper into these views, since according to our opinion the idea of the selective transmission can in no way explain the selective photoeffect. For a selective photoeffect it is not strictly necessary to have any metal layer at all; fluoride, hydride or oxide layers on glass or quartz as underlayer can give a selective photoeffect with the atoms adsorbed on their surfaces. In these cases there can be no conduction electrons emitted from a metal and they cannot thus be selectively allowed to pass through a layer on the surface.‡

\* W. H. Zachariasen, *Phys. Rev.* **38**, 2290 (1931).

† J. Frenkel, *Phys. Rev.* **38**, 309 (1931).

‡ Cf. J. H. de Boer, *Chem. Weekblad*, **29**, 34 (1932).



Further it is difficult to see how the high yield of electrons per absorbed quantum of light, which is so characteristic of the selective photoeffect (see also § 66), can be ascribed to a selective transmission for electrons, since the transmission coefficient for pure metal surfaces is already practically unity (§ 4).\*

In spite of the fact that the selective photoeffect may not primarily be ascribed to a selective transmission of electrons, it is still possible that a formula quite similar to that derived by Fowler and used by Olpin plays a certain part.†

As was stated above according to the view of Suhrmann the alkali metal atoms must be adsorbed or bound to an intermediate layer. Since a selective photoeffect can also be observed in the adsorption on pure metal surfaces, it was later assumed that a first monatomic layer of alkali metal can play the part of such an intermediate layer.‡ At the same time it is assumed that the selective photoeffect in this case first appears when the covering of the surface is so great that the minimum of the work function has already been passed, which point is identified with the completion of the first monatomic adsorbed layer. Now we have seen (see, for example, § 70) that the selective photoeffect already appears or can appear as soon as atoms are adsorbed, and certainly also with atoms which are adsorbed directly on the metal.

An intermediate layer is thus quite unnecessary, and we arrive at the condition already mentioned in previous sections: *adsorbed atoms are necessary and sufficient for the selective photoeffect*. Photoionization of these adsorbed atoms is the cause of the selective photoeffect. The spectral selectivity is only an expression of the spectral position of the absorption band of the adsorbed atoms; the vectorial selectivity for || light may be ascribed to the fact that only such light is absorbed (§ 64).

After the photoionization of atoms adsorbed on metal surfaces, the ions formed may be neutralized immediately by

\* Cf. L. B. Linford, *Rev. Mod. Phys.* **5**, 57 (1933).

† J. H. de Boer and M. C. Teves, *Z. Phys.* **83**, 530 (1933).

‡ R. Suhrmann and A. Schallamach, *Z. Phys.* **79**, 153 (1932).

electrons from the supporting metal; in the adsorption on dielectrics this provision of electrons must take place through the dielectric layer, which therefore must not be too thick (§ 65). Photoelectric phenomena in the presence of a thicker intermediate layer will be discussed later (Chap. XIII). It is for this supplying of electrons that a formula similar to that of Fowler for the selective transmission may play a certain part, but then indeed only for intermediate layers of at least several atoms thickness, and not for the monatomic coverings for which Fowler deduced his formula.

## CHAPTER X

### ALKALI METAL ATOMS ADSORBED WITHIN THE LATTICE OF THE ALKALI HALIDES, AND THEIR PHOTOELECTRIC PROPERTIES

#### § 72. Introduction.

In previous chapters we have discussed among other subjects the adsorption of alkali metal atoms on metal surfaces (Chaps. III, IV, V, VI and IX), as well as the adsorption of alkali metal atoms on the surface of dielectrics as halides, oxides and so on (Chaps. VIII and IX). Especially in Chaps. V and IX we have seen that upon the absorption of light by such adsorbed atoms electrons are emitted—selective photoelectric effect—in which process the atoms are converted into positive ions. In this chapter we shall discuss the adsorption of alkali metal atoms *within* dielectrics, whereby the adsorbed atoms are not found on the boundary surface between the dielectric and a vacuum, but in contrast are surrounded on all sides by the dielectric. We must, however, continually keep in mind that in this internal adsorption the dielectric will not form a completely symmetrical environment for the adsorbed atoms, but that the atoms will be adsorbed on internal surfaces, places of disturbance, crystal imperfections, irregularities of the regular lattice or foreign atoms. We shall continually see that these irregularities, which are generally indicated in German by the term “Lockerstellen”, play a very important part in this subject.

We shall see further that the absorption of light by these internally adsorbed atoms, just as that of atoms adsorbed on external surfaces, leads to photoionization, with this one difference, that in the case now under consideration the electrons freed are not emitted into the vacuum but into the crystal lattice of the dielectric. This difference has a very great influence on the energy connected with the process of photoionization. Electrons of any arbitrary energy cannot be introduced into the lattice of a dielectric, as they may be into a

vacuum. Electrons can only move about in such a lattice if their energy fulfils certain very definite conditions, which are given by the structure of the lattice. Because of this fact a portion only of the continuous energy spectrum which would be possible if the atoms under consideration were adsorbed on an external surface occurs, while the rest does not, thus giving in many cases a relatively simple form to the energy spectrum, and consequently also to the frequency spectrum which is connected with it.

The emission of electrons from the atoms adsorbed internally in the lattice and the movement of these electrons in an electric field are manifested as a photoelectric conduction of a compound which may or may not possess conductivity when unilluminated. We must examine various problems which are connected with the photoelectric conductivity, but only in so far as they are connected with the problems of this book.\*

We shall further see (Chap. XI) that in very many cases the internally adsorbed atoms can also give up their electrons under thermal influences. This thermal ionization which leads to an electrical conduction is essentially similar to the thermal ionization of atoms adsorbed on external surfaces, a phenomenon which is the fundamental cause of the thermionic emission of many electron-emitting cathodes built up of dielectrics (Chap. XIV).

In the following sections we shall first examine the methods by which alkali metal atoms can be introduced into lattices of alkali metal compounds, and afterwards we shall investigate in more detail the properties of these internally adsorbed atoms.

### § 73. The absorption of light by pure alkali halides.

The crystals of the alkali halides are completely transparent in the visible and near ultraviolet spectral regions. Light absorption is found only in the relatively far ultraviolet, and takes the form of very pronounced, sharp and strong absorp-

\* For a good survey of photoelectric conduction see: B. Gudden, *Lichtelektrische Erscheinungen*, Chaps. X, XI, XII and XIII (1928); A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, Chap. VIII (1932); F. C. Nix, *Rev. Mod. Phys.* 4, 723 (1932).

tion bands. On the basis of accurate measurements of the indices of refraction it was known before 1929 approximately where the absorption bands of the alkali halides must lie.\* The excellent investigations of Hilsch and Pohl showed the exact position and structure of the absorption bands. Hilsch and Pohl† measured very accurately the absorption of light of the alkali halides in the form of thin layers obtained by sublimation in a high vacuum, thus of layers similar to those discussed in § 59. The maxima of the first absorption bands in the case of the iodides lay at about  $220\text{m}\mu$ , in the case of the bromides at about  $190\text{m}\mu$ , and in the case of the chlorides at about  $160\text{m}\mu$ . The fluorides are transparent still farther into the ultraviolet; by means of the electron collision method (method of Franck and Hertz, see § 11), applied here to the solid alkali halides, Hilsch‡ found the first maxima for lithium fluoride at about  $107\text{m}\mu$ , for sodium fluoride at about  $134\text{m}\mu$  and for calcium fluoride at about  $119\text{m}\mu$ .

In § 55 we saw that in the absorption of light of the alkali halide molecules in the gaseous state an electron jumps from the negative halogen ion to the positive alkali metal ion, giving rise to a molecule built up out of atoms, which immediately breaks up into atoms again. In the case now under consideration a transition of an electron from the halogen ion to the alkali ion of the lattice immediately next to it also takes place upon the absorption of light. When we attempt to calculate the energy which must be added to make this electron jump possible, we must remember that the electron affinity of the halogen ion,  $E$ , must be overcome and that the work of ionization,  $I$ , is regained in the neutralization of the alkali metal ion. In addition two charges disappear within the lattice, so that work must be done against the Coulomb attraction forces of these charges. Hilsch and Pohl assumed that for the neutralization of these charges in the lattice an amount of energy was required equal to the electrostatic part of the lattice energy:

\* K. F. Herzfeld and K. L. Wolf, *Ann. Phys.*, Lpz., **78**, 35 (1925).

† R. Hilsch and R. W. Pohl, *Z. Phys.* **57**, 145 (1929); **59**, 812 (1930).

‡ R. Hilsch, *Nachr. Ges. Wiss. Göttingen*, p. 203 (1931); *Z. Phys.* **77**, 427 (1932).

$A_M \frac{\epsilon^2}{d}$  (see § 12), so that the position of the absorption band would be given by the relation

$$h\nu = E - I + A_M \frac{\epsilon^2}{d}.$$

This relation actually represents the position of the first absorption bands remarkably well, although the calculation of the energy necessary for the neutralization of the two charges in the lattice is not correct. If one ion (the halogen ion) is neutralized within the lattice, an amount of energy  $A_M \frac{\epsilon^2}{d}$  is necessary; the neutralization of another ion (the alkali metal ion) in the lattice would require the same amount again, if this ion were also surrounded on all sides by charges. If, however, an alkali metal ion is neutralized which lies immediately next to the halogen ion which loses its electron, only a quantity of energy  $(A_M - 1) \frac{\epsilon^2}{d}$  is necessary for the neutralization of this alkali atom, since one of the neighbouring ions (one  $\frac{\epsilon^2}{d}$  term) was no longer present (the halogen ion was already neutralized). We arrive at the result that the expected position of the absorption band is given by the relation

$$h\nu = E - I + (2A_M - 1) \frac{\epsilon^2}{d}.$$

This relation was derived by Wolf and Herzfeld;\* it does not however represent very well the experimentally found value of  $h\nu$ , a fact which will have occurred to the reader considering the fact that the theoretically less correct formula used by Hilsch and Pohl did give good results. With lattices of the type of sodium chloride,  $A_M$  (the Madelung constant) is equal to 1.747 (§ 12), so that the difference between the two formulae is  $\frac{0.747 \epsilon^2}{d}$ , with the result that the theoretically better formula gives results which are about 30 per cent. too high.

\* K. L. Wolf and K. F. Herzfeld, *Handbuch der Physik* (Geiger-Scheel), 20, 632 (1928).

In this connection another explanation has been sought for the mechanism of this absorption of light. The possibility has been considered that this absorption of light is not given by all the ions of the lattice, but that here again the internal disturbances (Lockerstellen) may play a part. Thus Born\* came to the conclusion that in this light absorption it is not two ions lying next to each other in the lattice which are neutralized, but a pair of ions upon an internal surface. If, however, only ions lying on internal surfaces should serve as absorption centres, it is quite impossible to understand why the absorption bands which are found are so strong (see also § 76). For that reason Born assumed that a halogen ion *within* the lattice serves as a centre of absorption, and gives up its electron upon absorption, whereupon this electron moves through the lattice to an alkali metal ion at a place of disturbance and neutralizes this. There are many serious objections to this conception, of which we shall only mention two. If this conception were correct, electrons would be moving through the lattice during absorption; Hilsch and Pohl† were, however, unable to discover any movement of electricity at all in this absorption of light, which is in contrast to the absorption of light by salts such as the silver and thallium halides which we shall treat later (§ 86). The second objection is that Born's conception is quite contrary to the Franck-Condon principle (§ 54).

For the explanation of the absorption of light by these lattices the co-operation of the internal surfaces is not necessary. We have already seen in Chap. VIII that the adsorption energy may play an important part in light absorption processes. It is true in this case too; the two atoms formed here in the primary process of light absorption are bound in the lattice at the spot where they are formed. The gain in energy which accompanies this internal adsorption makes the process of absorption easier and is one of the reasons why the experimentally found absorption bands are at longer wave-lengths than the formula of Wolf and Herzfeld would lead one to

\* M. Born, *Z. Phys.* **79**, 62 (1932).

† R. Hilsch and R. W. Pohl, *Z. Phys.* **68**, 721 (1931).

expect.\* Klemm† called attention to the fact that because of the formation of two electrically neutral atoms the ions are no longer completely symmetrically surrounded by charges; these ions are polarized in one direction, which polarization again is the source of an important gain in energy. Finally the value of  $h\nu$  for the absorption bands may be calculated from the following formula:

$$h\nu = E - I + (2A_M - 1) \frac{\epsilon^2}{d} - \Psi_{\text{pol.}} - \Omega_{\text{hal.}} - \Omega_{\text{alk.}}$$

In this equation  $E$  is the electron affinity of the halogen,  $I$  is the ionization energy of the alkali metal atom.

$$(2A_M - 1) \frac{\epsilon^2}{d} = 2.494 \frac{\epsilon^2}{d}$$

is the work necessary to remove two charges next to each other in the lattice,  $d$  is the shortest distance between two dissimilarly charged ions in the lattice.  $\Psi_{\text{pol.}}$  is the gain in energy due to the polarization of the surrounding ions; for this term, according to a calculation which Born had carried out in consequence of the article by Klemm, one may write

$$\Psi_{\text{pol.}} = 2.027 \frac{\epsilon^2}{d^4} (\alpha_1 + \alpha_2),$$

in which  $\alpha_1$  and  $\alpha_2$  are the polarizabilities of the two kinds of ions in the lattice (valid for the NaCl type).  $\Omega_{\text{hal.}}$  is the adsorption energy of the halogen atom formed in the lattice, and may be set equal to  $\frac{1}{2} \frac{\epsilon^2}{d^4} \alpha_{\text{hal.}}$ , where  $\alpha_{\text{hal.}}$  is the polarizability of the halogen atom.  $\Omega_{\text{alk.}}$  is the corresponding adsorption energy of the alkali metal atom formed in the lattice, for which, through lack of a better method of calculation,  $\sqrt{S_{\text{alk.}} \times S_{\text{salt}}}$  may be written, where  $S_{\text{alk.}}$  and  $S_{\text{salt}}$  are the energies of sublimation of the alkali metal and of the salt. In this last expression, which is analogous to the one used in the adsorption of a caesium or barium atom on a tungsten surface (§§ 27 and 32), there is no factor  $\frac{1}{2}$  before the radical as there was in the

\* J. H. de Boer, *Z. phys. Chem. B*, **18**, 49 (1932).

† W. Klemm, *Z. Phys.* **82**, 529 (1933).



previous case, since here the alkali atom is surrounded on all sides by the lattice. The calculated and observed values are given in Table VIII. It can be seen from the table that the calculation gives the correct order of magnitude, so that we may accept as valid the explanation of the mechanism of this light absorption as a transition of an electron from a halogen ion in the lattice to an alkali ion lying next to it.

Table VIII. *The first absorption band of the alkali halides, calculated and observed*

Energies in electron volts

Salt	$\frac{E - I + (2A_M - 1)}{\epsilon^2 \bar{d}}$	$\Psi_{\text{pol.}}$	$\Omega_{\text{hal.}}$	$\Omega_{\text{alk.}}$	$h\nu_{\text{calc.}}$	$h\nu_{\text{exp.}}$	Max. of absorption band in $m\mu$
NaCl	11.3	1.6	0.3	1.8	7.6	>7.70	<160
KCl	10.9	1.3	0.2	1.6	7.8	7.60	162.5
RbCl	10.5	1.2	0.1	1.6	7.6	7.40	167
LiBr	11.1	2.2	0.4	2.0	6.5	6.67	185
NaBr	10.4	1.7	0.3	1.7	6.7	6.50	190
KBr	10.1	1.4	0.2	1.6	6.9	6.58	187.5
RbBr	9.8	1.4	0.2	1.5	6.7	6.43	192
LiI	9.6	2.2	0.4	1.9	5.1	5.59	221
NaI	9.2	1.8	0.3	1.6	5.5	5.39	229.5
KI	9.0	1.4	0.2	1.6	5.8	5.63	219
RbI	8.8	1.4	0.2	1.5	5.7	5.55	222.5

We have seen previously in § 55, that in the case of the vapours of the alkali halides more absorption bands follow the first one farther into the ultraviolet. The elementary reaction connected with these bands is such that one of the atoms formed is in an excited state. A similar circumstance is met with in the case of the solid salts. The first band of the iodide is followed by a second whose  $h\nu$  value is about 1 electron volt higher, so that it may be assumed that upon irradiation within this band the resulting products are one neutral alkali metal atom and one excited, metastable iodine atom. The second band of the iodides is followed again by a third in which an excited alkali metal atom is formed as a product of the reaction. In the case of the bromides the first band is followed by

second, to which corresponds a quantity of energy 0.5 electron volt higher than that of the first (see Fig. 96 for KBr).

At lower temperatures the absorption bands become sharper and are shifted toward shorter wave-lengths; upon increase of temperature the reverse takes place.\* Thus the first absorption band of KI (see Table VIII) at room temperature lies at  $219\text{m}\mu$ , at  $-253^\circ\text{C}$ . at  $210\text{m}\mu$ , at  $+220^\circ\text{C}$ . at  $227\text{m}\mu$ .

The absorption spectra of the alkali cyanides and the alkali thiocyanides are similar in structure to those of the alkali halides. Thus KCN has a sharp absorption band at  $196\text{m}\mu$ , KCNS at  $183\text{m}\mu$ .†

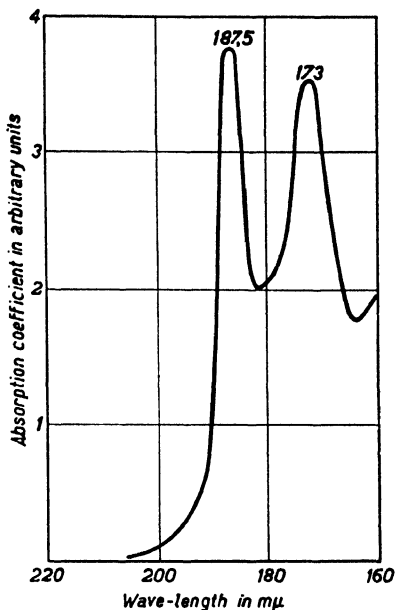


Fig. 96. Absorption of light by pure KBr. R. Hilsch and R. W. Pohl, *Z. Phys.* 59, 817 (1929).

#### § 74. The introduction of adsorbed alkali metal atoms in the lattice of their salts by photochemical means.

The elementary process of light absorption by the salts of the alkali halides is thus a transition of an electron from a halogen ion in the lattice to an adjacent alkali metal ion, in which process both ions are transformed into atoms. Such a state is quite unstable in the lattice and the electron must immediately jump back again. A lasting number of alkali metal atoms cannot be obtained in this way. Still the originally colourless crystal becomes coloured by illumination with light lying within the absorption band, and alkali metal atoms are formed in the lattice which cause the appearance of their own characteristic absorption of light.‡ Thus in sodium chloride

\* H. Fesefeldt, *Z. Phys.* 64, 623 (1930).

† H. Fesefeldt, *Nachr. Ges. Wiss. Göttingen*, p. 353 (1923).

‡ R. Hilsch and R. W. Pohl, *Z. Phys.* 64, 606 (1930); 68, 721 (1931).

sodium atoms are formed by its irradiation with light lying within the short wave-length absorption band at about  $160\text{m}\mu$ , and the salt is coloured yellow (new absorption band of the internally adsorbed sodium atoms at  $465\text{m}\mu$ ). We must assume that these built-in sodium atoms are adsorbed on internal surfaces or defects or the crystal structure. Because of this latter fact the amount of sodium atoms which can be built into a sodium chloride lattice varies for various lattices, since the number of "Lockerstellen" (see § 72) varies. The chlorine atoms formed at the same time must also be adsorbed on internal surfaces, but they do not give rise to an absorption band in the normal spectral range. These halogen atoms must be assumed to have moved a certain distance away while still remaining on the internal surface where they are formed (§ 78).

According to the very detailed and systematic research by Smekal\* the various physical *properties* of crystal lattices can be divided into two large groups. (1) Those connected with the internal structure, dependent upon the number and the type of the "Lockerstellen", and which change upon mechanical deformation of the lattice. This group may be called the *properties sensitive to structure*. (2) Those properties which represent true material properties and which are not directly dependent upon defects in the crystal structure and similar circumstances. The second group may be called the *properties insensitive to structure*. While the absorption of light of the pure lattices, as it was discussed in the previous section, belongs in principle to the properties of the second group, all properties connected with built-in alkali metal atoms are sensitive to structure,† so that defects of the crystal structure on internal surfaces must play a great part in these cases.

We must then also assume that only the absorption of light by ions on internal surfaces or places of disturbance leads to the formation of a lasting amount of alkali metal adsorbed in-

\* Cf. A. Smekal, *Atti del Congresso Internazionale dei Fisici*, Como (1927); *Z. Elektrochem.* **34**, 472 (1928); *Z. Phys.* **55**, 289 (1929); *Phys. Z.* **33**, 204 (1932); *Handbuch der Physik* (Geiger-Scheel), 2e Auflage, **24**, 2, pp. 795-923 (1933).

† Compare A. Smekal, *Phys. Z.* **33**, 204 (1932); H. J. Schröder, *Z. Phys.* **76**, 608 (1932).

ternally. Now Smakula\* discovered that at the beginning of this photochemical process one alkali metal atom is formed for each quantum of light absorbed. At first glance that is absolutely contrary to our expectation, which was that the absorption of light by the lattice ions does not lead to a lasting formation of alkali metal atoms. It must, however, be kept in mind that Smakula does not use light at the maximum of the absorption band but light within the extension of this band toward longer wave-lengths, where the absorption is very much weaker. According to his description this illumination within the long-wave extension of the absorption band is a necessary condition for the success of the experiments. Now the light absorption in the long-wave extension is probably entirely dominated by the absorption of the ions lying at points of disturbance of the lattice. In his illumination of potassium bromide, for example, the maximum of whose absorption band lies at  $187.5\text{ m}\mu$  (see Fig. 96), Smakula uses light of  $203\text{ m}\mu$ ,  $199\text{ m}\mu$  and  $193\text{ m}\mu$ . If one were able to make a completely ideal crystal without any defects of the lattice (such crystals cannot be made), then perhaps such a crystal of potassium bromide would exhibit no absorption at all at  $203\text{ m}\mu$ , and would not become coloured by irradiation with this wave-length. The more places of disturbance a crystal has and the more foreign ions or foreign components a lattice possesses, the more pronounced is the long-wave extension of the absorption band.† Hilsch and Pohl were able to trace the influence of the extension of the absorption band, which is ascribed to defects in the lattice, into the visible spectral region in the case of potassium bromide. The absorption of light has then become so small that a crystal 5 kilometres thick would decrease the intensity of the light by  $\frac{1}{e}$  (37 per cent.).

As has been already stated, Smakula discovered that in the beginning one internally adsorbed alkali metal atom is formed for each quantum of light absorbed. Under continued illumination this good yield decreases quickly, and saturation is

\* A. Smakula, *Z. Phys.* **63**, 762 (1930).

† R. Hilsch and R. W. Pohl, *Z. Phys.* **68**, 721, 731 (1931).

finally reached, that is to say, under continued illumination no more alkali metal atoms are formed. The number of alkali metal atoms present at saturation, besides being dependent upon the number of defects of the crystal structure, etc., and the temperature, depends also upon the wave-length of the light used for irradiation. This dependence upon wave-length is such as could be expected from the picture developed above, namely, the number of alkali metal atoms present at saturation point is smaller the shorter the wave-length of the light used, thus the closer it is to the maximum of the absorption band of the ions in the lattice. When saturation is reached the absorption band of the lattice is of course still present and unchanged. If care is taken to provide very many places of disturbance in the crystal, the number of alkali metal atoms which can be formed in the lattice by photochemical means is extraordinarily large. Thus the number of alkali metal atoms per unit volume in a salt layer obtained by sublimation may be more than 1000 times as great as in a carefully prepared crystal of the same compound.\* We have already seen in § 59 that such salt layers have a very large external surface, and they are probably very well provided with internal surfaces. Especially when they have been subjected to a sintering process (§ 60, the alkali halides are very easily sintered) the *internal* surface is very great.

The number of alkali metal atoms which can be adsorbed in the lattice on internal surfaces varies in addition with the previous thermal or mechanical treatment of the crystal and is thus typically a property sensitive to structure.† Crystals which have grown rapidly or have been formed by sudden cooling are able to contain more alkali metal atoms than those which have grown slowly.

#### § 75. Other methods for the introduction of internally adsorbed alkali metal atoms.

In addition to the above-described photochemical method, alkali metal atoms can also be introduced into the lattice by

\* R. Hilsch and R. W. Pohl, *Z. Phys.* **64**, 606 (1930).

† E. Goldstein, *Berl. Ber.* p. 22 (1901); K. Przibram, *Z. Phys.* **68**, 403 (1931).

other means; for example by illuminating with X-rays, by exposing to radioactive radiation, by bombarding with electrons, by allowing electrons to enter a warmed crystal from a pointed electrode, or by heating the crystals in the vapour of alkali metals. We shall return to the last two methods in some of the succeeding sections (§§ 81 and 82).

In the heating of the crystal of alkali halide in the vapour of alkali metal (additive colouring method) it appears as if the alkali metal atoms diffuse directly into the lattice, and are there adsorbed upon internal surfaces. The properties of the alkali metal atoms introduced into the lattice in this way are identical with those introduced by the photochemical method.\*

The investigation of Rexer† on the additive colouring have confirmed its sensitivity to structure. The quantitative behaviour and the final result of the diffusion of the alkali metal atoms into the lattice are very dependent upon the previous history of the crystal, that is to say, upon the number and character of the internal places of disturbance, or internal surfaces upon which the alkali metal atoms are adsorbed. Very often small particles of alkali metal with colloidal dimensions are formed by the coagulation of the alkali metal atoms in the lattice, which particles have quite different optical and electrical properties than those of the internally adsorbed alkali metal atoms (§ 84). In crystals which have been made homogeneous by a temperature treatment these colloidal particles are very easily formed; atomic distributions are easiest to obtain in crystals formed by sudden cooling which are provided with many coarse defects of structure. It also appears very clearly from Rexer's experiments that the "diffusion" of the alkali metal into the lattice is no ordinary diffusion. It is a very striking fact that when a crystal is coloured by allowing alkali metal atoms to penetrate from one side only, and if the process is stopped when the crystal is partially coloured, then if afterwards the crystal is still kept at the same temperature but now in the absence of alkali metal vapour, the alkali metal atoms do not become homogeneously distributed over the

\* Z. Gyulai, *Z. Phys.* **37**, 889 (1926).

† E. Rexer, *Z. Phys.* **70**, 159 (1931); **76**, 735 (1932); **86**, 1 (1933).

lattice, as should happen in real diffusion, but they disappear out of the crystal by the same path as that by which they entered it.\* We shall see in § 82 that the mechanism of this additive colouring is in reality a penetration of electrons into the lattice, which electrons transform alkali metal ions at places of disturbance into alkali metal atoms.

Mollwo† systematically investigated the number of alkali metal atoms which can be taken up by the lattice at various temperatures, and came to the conclusion that at each temperature there is an equilibrium concentration of internally adsorbed atoms. Excess atoms coagulate to colloid particles. This equilibrium concentration is only reached after a sufficiently long time of establishment; its variation with temperature has the character of a vapour-pressure curve. Mollwo is even inclined to compare the equilibrium concentration with the vapour pressure of the alkali metal concerned. The equilibrium concentration is merely a minimum value which can easily be exceeded by all kinds of defects of crystal structure, for example, which are able to increase the concentration by more than 1000 times. Defects of the crystal structure thus act in the same way as increase of temperature.‡ One might now ask why there should be a definite equilibrium concentration at every temperature, even when there are no disturbances of the lattice. As we have already mentioned (§ 74) alkali metal atoms cannot exist within the lattice, but must be adsorbed on internal surfaces or defects. In an ideal crystal without defects or internal surfaces it should be impossible to introduce alkali metal atoms. However such an ideal crystal does not exist. According to Zwicky a secondary structure is superposed upon the fundamental lattice of any actual crystal.§ This secondary structure consists of blocks whose dimensions lie between 100 Å. and 10,000 Å. and which are arranged very regularly.

\* E. Rexer, *Phys. Z.* **32**, 215 (1931).

† E. Mollwo, *Z. Phys.* **85**, 56 (1933).

‡ Cf. also: W. Flechsig, *Z. Phys.* **36**, 605 (1926); R. Hilsch and R. W. Pohl, *Nachr. Ges. Wiss. Göttingen*, p. 406 (1933).

§ F. Zwicky, *Proc. Nat. Acad. Sci., Wash.*, **15**, 816 (1929); *Helv. Phys. Acta*, **3**, 269 (1930); **4**, 49 (1931); **6**, 210 (1933); *Phys. Rev.* **38**, 1772 (1931); **40**, 63 (1932); H. M. Evjen, *Phys. Rev.* **34**, 1385 (1929); **39**, 675 (1932); **41**, 285 (1932); **44**, 491, 501 (1933).

Although there are objections to the calculations of Zwicky\* such a secondary structure is very possible and it is probably connected with the polarizability of the ions or atoms of the lattice. If we assume that the alkali metal atoms are adsorbed at the corners of the blocks of this secondary structure and that the size of these blocks decreases with rising temperature—which is a very probable assumption—then we would be able to understand the “equilibrium concentration” found by Mollwo. A linear dimension of block of  $100\text{ \AA}$ . would give a concentration of  $10^{18}$  atoms per  $\text{cm}^3$  if there were one atom adsorbed per block. Mollwo found in the case of potassium bromide at above  $500^\circ\text{C}$ . such an equilibrium concentration. It is however still possible that the alkali metal atoms present at the “equilibrium concentration” are adsorbed upon foreign ions or upon the places of disturbance caused thereby, or upon other internal surfaces. One of the highest equilibrium concentrations reached by Mollwo ( $10^{18}$  atoms/ $\text{cm}^3$ ) means in this respect only that there is a place of disturbance every  $100\text{ \AA}$ . in each direction in the lattice. Less than 0.01 per cent. of impurities is sufficient to give this number of places of disturbance.†

### § 76. Photoionization of the internally adsorbed alkali metal atoms.

As was stated in the previous sections the presence of internally adsorbed alkali metal atoms causes a coloration, and thus these alkali metal atoms are frequently called “colour centres”, which name we shall also use. In every crystal the colour centres give a very characteristic absorption band‡ of simple form. In Fig. 97 the absorption spectra are drawn of potassium atoms which are adsorbed internally in potassium fluoride, potassium chloride, potassium bromide and potas-

\* Cf. A. Smekal in *Handbuch der Physik* (Geiger-Scheel), 2e Auflage, 24, 2, pp. 803–5 (1933); E. Orowan, *Z. Phys.* 79, 573 (1932); *Helv. Phys. Acta*, 7, 285 (1933).

† In  $\text{CaF}_2$  much higher values may occur, cf. foot-note \* on page 350.

‡ K. Przibram, *Phys. Z.* 25, 640 (1924); P. L. Bayley, *Phys. Rev.* 24, 495 (1924); Z. Gyulai, *Z. Phys.* 32, 103 (1925); 33, 251 (1925); 35, 411 (1926); W. Flechsig, *Z. Phys.* 36, 605 (1926); R. Ottmer, *Z. Phys.* 46, 798 (1928); A. Smakula, *Z. Phys.* 63, 762 (1930).



sium iodide, while in Table IX the position of the maxima in various cases is given. In § 85 we shall return to examine the regularity in the position of these maxima. The maxima of the colour centres (Fig. 97) are much lower than the ultraviolet absorption of the lattices themselves (§ 73); the relation is for instance 1 to  $10^6$ , in agreement with the ratio between the number of absorbing colour centres and of the ions of the lattice itself.

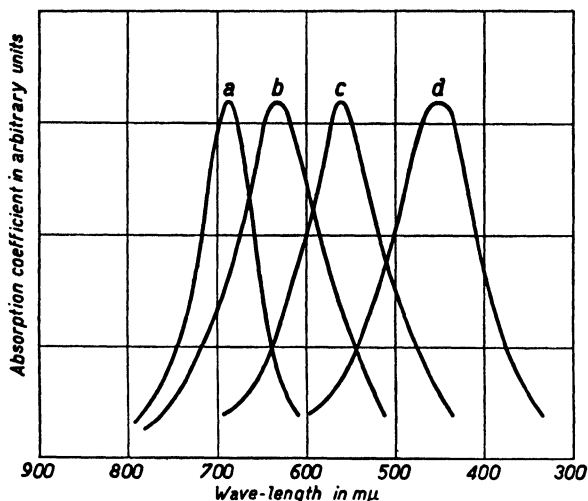


Fig. 97. Absorption of light by potassium atoms, adsorbed at internal surfaces in the lattices of *a*: KI; *b*: KBr; *c*: KCl; *d*: KF. Cf. R. Ottmer, *Z. Phys.* **46**, 798 (1928).\*

Table IX. *Position of the absorption maxima of the alkali metal atoms in their salts\**

Salt	$\lambda$ in $m\mu$	Energy in electron volts	Salt	$\lambda$ in $m\mu$	Energy in electron volts
LiF	250	4.95	KF	455	2.71
LiCl	385	3.20	KCl	563	2.19
NaF	340	3.63	KBr	630	1.96
NaCl	465	2.65	KI	685	1.80
NaBr	540	2.29	RbCl	624	1.98
NaI	588	2.10	RbBr	720	1.71
			RbI	775	1.59

\* E. Mollwo, *Nachr. Ges. Wiss. Göttingen*, p. 97 (1931); *Z. Phys.* **85**, 62 (1933).

Upon increase of temperature the maximum shifts toward longer wave-lengths and the band becomes broader and flatter, at lower temperatures the maximum shifts toward shorter wave-lengths and the band becomes narrower and higher.\* Fig. 98 gives the temperature dependence for the colour centres in potassium bromide. With each salt, according to the experiment of Mollwo, there is one wave-length (with KBr,  $\lambda_p = 572 m\mu$ ) at which, regardless of the temperature, the absorption is one-half of the maximum.

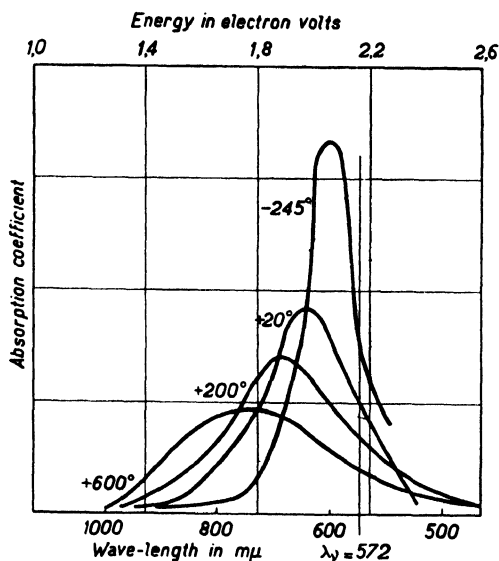


Fig. 98. Absorption spectrum of potassium atoms in KBr at different temperatures. E. Mollwo, *Z. Phys.* **85**, 62 (1933).

The absorption band is broadened not only by an increase of temperature, but also by the presence of many crystal imperfections. Thus the absorption band of coloured synthetic rock-salt crystals is broader than that of the more perfect crystals of coloured natural rock-salt.†

Upon the absorption of light within this absorption band of the colour centres an electron is split off the alkali metal atom.‡

\* R. Hilsch and R. W. Pohl, *Z. Phys.* **64**, 606 (1930); E. Mollwo, *Nachr. Ges. Wiss. Göttingen*, p. 236 (1931); *Z. Phys.* **85**, 61 (1933).

† W. Flechsig, *Z. Phys.* **36**, 605 (1926).

‡ B. Gudden and R. W. Pohl, *Z. Phys.* **31**, 651 (1925); cf. also B. Gudden, *Lichtelektrische Erscheinungen*, pp. 164 ff. (1928).

As in all phenomena of the selective photoeffect (Chap. IX) here also an adsorbed atom (in this case internally adsorbed) is ionized by the absorption of light, so that the absorption band is at the same time the photoionization band. There is here no suggestion of excited states of the adsorbed atom any more than was the case in the adsorption on external surfaces; the whole absorption leads to ionization. In the case under consideration the electron is however not emitted to the outside but within the lattice. If the salt crystal is placed between two electrodes (Fig. 99) these liberated electrons move in the lattice toward the side of the anode and a photoelectric conduction current is measured. This "primary photoelectric current" sets in at its full value the instant the light is turned on, while the values at the start are strictly proportional to the intensity of the light.\* In the absence of an electric field the electrons move a distance of several atomic diameters in an arbitrary direction in the lattice; in an electric field they are drawn towards the anode. Now the electron does not pass through the whole lattice, but only until it meets an obstacle, that is to say a discontinuity in the lattice, a submicroscopic crack or an internal surface. By this movement the electrons cover an average distance  $x$  (see Fig. 99), which distance increases proportionally with the field. The current measured is equal to

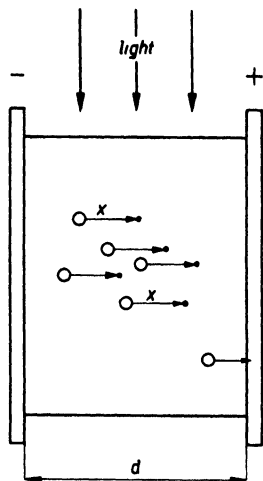


Fig. 99. The electrons released by light from the internally adsorbed atoms move a distance  $x$  toward the anode.

$$i = n\epsilon \frac{x}{d},$$

where  $n$  is the number of electrons liberated per second by the light,  $\epsilon$  is the absolute value of the charge of an electron and  $d$  is the total thickness of the crystal (distance between the electrodes). Since  $x$  increases proportionally with the electric

\* W. Flechsig, *Z. Phys.* **33**, 372 (1925).

field, the current increases proportionally with the field strength as long as  $x$  is small with respect to  $d$ . Because of this fact it appears as if Ohm's law were followed. It follows from measurements by Gyulai\* that in yellow rock-salt in a field of 2000 volts/cm. the electrons cover a distance of about  $3 \times 10^{-4}$  cm. in the lattice. If  $x$  becomes so large (or  $d$  so small) that all the electrons can be drawn completely through the crystal, the current of course no longer increases with the tension; all the electrons freed by the light are simply attracted to the anode and the current is saturated. Saturation values can thus be reached at high field strengths and small thicknesses of the crystal. Flechsig† obtained saturation currents by the illumination of yellow salt of 0.1 mm. thickness in a field of about 50,000 volts/cm.

Just as in the selective photoeffect (Chap. IX) one electron is freed for every quantum of light absorbed. Since with decreasing wave-length of light a light quantum represents a larger amount of energy, the result is that on the short-wave

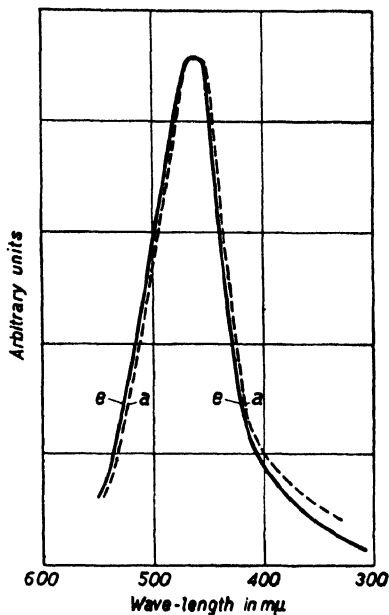


Fig. 100. Absorption spectrum (a) and photoelectric current (e) per unit incident light.‡

side of the absorption band of the alkali metal atoms in the lattice the yield of electrons for a definite quantity of absorbed energy is somewhat smaller than on the long-wave side. Fig. 100 gives the spectral distribution of the light absorption and the spectral distribution of the primary photocurrent (referred to incident energy) as they are measured by Gyulai.‡ The small shift with respect to each other exhibited by the

\* Z. Gyulai, *Z. Phys.* **32**, 103 (1925).

† W. Flechsig, *Z. Phys.* **46**, 788 (1928).

‡ Z. Gyulai, *Z. Phys.* **32**, 105 (1925).

curves illustrates very well the quantum equivalence. This small shift of the curves is disputed by Arsenjewa;\* she maintains that the photoelectric current is strictly proportional to the energy absorbed.

Upon increase of temperature the spectral distribution of the photoelectric current shifts simultaneously with that of the absorption of light (see Fig. 98 above) toward longer wavelengths,† and it thus requires less energy on the average to free an electron from the internally adsorbed alkali metal atoms. With reference to absorbed energy the starting values of the primary photoelectric current are independent of the temperature.

### § 77. Excitation of coloured crystals of the alkali halides.

In the previous section we saw that the electrons liberated from the internally adsorbed alkali metal atoms by the absorption of light move over a definite distance through the lattice and then remain fixed at a crystal imperfection, an internal surface or a foreign atom. The originally neutral atoms remain as positive ions, while the electrons give a negative charge at the spots where they have become fixed. Hereby a space charge is created in the crystal which opposes the photoelectric current. If nothing further happens the photoelectric current decreases rapidly, especially at a low temperature and with a relatively intense illumination. At the spots where the electrons have become fixed they are much less tightly bound than originally on the adsorbed alkali metal atoms. Thus they can be loosened after remaining some time at room temperature and more quickly under the application of heat, and can then move on again over a certain distance in the lattice. Thus the space charge formed may be neutralized, for instance by heating in the dark, and the electrons then join again the positive alkali metal ions on the internal surfaces which were formed in the photoionization from the adsorbed alkali metal atoms, by which neutralization process adsorbed alkali metal atoms are re-created. The state reached after this

\* A. Arsenjewa, *Z. Phys.* **37**, 701 (1926).

† B. Gudden and R. W. Pohl, *Z. Phys.* **34**, 249 (1925).

junction is no different from the original state. In this freeing of the electrons and the consequent neutralization of the space charge the electrons (under the same field) move on the average over a distance through the lattice equal to that over which they had moved originally during the illumination. (One must keep in mind here that the average distance over which the electrons move in the lattice is in general small in comparison with the dimensions of the crystal itself, but large in comparison with the average separation of the colour centres.) The neutralization of the space charge gives therefore a second displacement of the electric charge just as great as occurred originally during the illumination and the building up of the space charge. Gudden and Pohl\* call the current which is the direct result of the freeing and displacement of the electrons from the internally adsorbed alkali metal atoms, and thus the direct photoemission in the lattice, "the negative part of the primary photoelectric current" or "the negative primary current". The current which accompanies the neutralization of the space charge they call "the positive part of the primary photoelectric current" or "the positive primary current". The terms positive and negative come from the time when it was thought that the electrons actually moved toward the anode under the illumination, and that a movement of the remaining positive charges as a whole toward the cathode (as in gas discharges) would neutralize the space charge formed. We have seen however that both components exist in electronic conduction; they are comparable with, for example, the immediate current of emitted electrons mentioned in § 71, and the current of electrons which neutralize the positive ions formed to supplement those emitted, with this difference, that in the photoelectric conduction in the lattices the emission is not into a vacuum but takes place in the lattice, and that an electron emitted originally from one colour centre during the positive primary current serves to supplement the electron emitted from another colour centre.

In the state where the electrons have become fixed and thus create their space charge, we shall, with Gudden and Pohl, say

\* Cf. B. Gudden, *Lichtelektrische Erscheinungen*, p. 147.

that the crystal is "excited". The electrons which have become fixed form "excitation centres".\* As was noted above the electrons at the excitation centres are much less tightly bound than to the internally adsorbed alkali metal atoms (colour centres). This is also manifested in the absorption spectrum; during the illumination of the coloured crystal within its absorption band, thus during the excitation, the absorption of the colour centres decreases in intensity (the

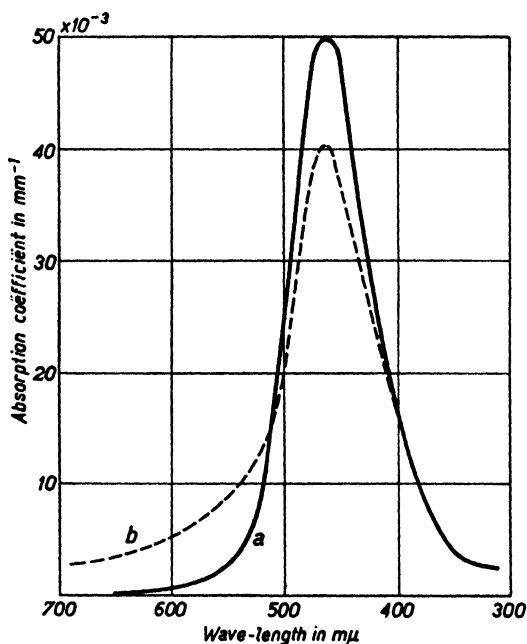


Fig. 101. Absorption spectrum of yellow rock-salt in the unexcited (*a*) and in the excited (*b*) state. Z. Gyulai, *Z. Phys.* **33**, 255 (1925).

number of internally adsorbed alkali metal atoms decreases), and a new absorption appears at longer wave-lengths. Thus curve *a* in Fig. 101 gives the absorption spectrum of yellow rock-salt in its non-excited state, while after illumination with blue light curve *b* is measured, the absorption spectrum in the excited state.† We may consider curve *b* as built up of a curve *c* (Fig. 102), which represents the absorption spectrum of the

\* Cf. B. Gudden, *Lichtelektrische Erscheinungen*, p. 149.

† Z. Gyulai, *Z. Phys.* **33**, 251 (1925).

remaining colour centres still unchanged after the illumination, and of a new curve *d*,\* the absorption spectrum of the excitation centres.

With respect to illumination the excitation centres behave exactly as the colour centres. Upon illumination with longer wave-lengths than were necessary for the appearance of the excitation (red or even infrared light may be used, see Fig. 102) the electrons are freed from the excitation centres and

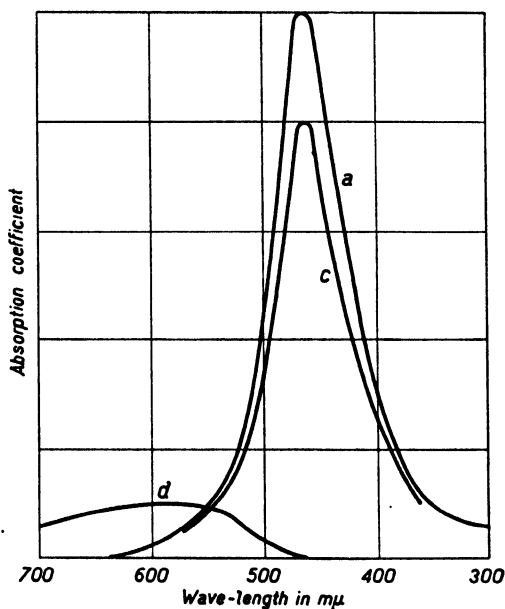


Fig. 102. Absorption spectra of the colour centres in yellow rock-salt before excitation (*a*), after excitation (*c*) and the absorption spectrum of the excitation centres (*d*).\*

emitted into the lattice; they move through the lattice and will in general end with the neutralization of a remaining positive ion of an original colour centre. Not only by the passage of time in the dark or by heating, but also by illumination with red or infrared light can the excitation be neutralized. Here again one electron per quantum of light is freed from the excitation centres. Thus the spectral distribution of the photoelectric conductivity of a crystal in the excited state is given

\* R. Hilsch and R. W. Pohl, *Z. Phys.* **68**, 721 (1931).



completely by its absorption spectrum (Fig. 101*b*), as was the case for non-excited crystals (Fig. 100).\*

When a yellow rock-salt crystal is irradiated with blue light and the temperature is not too high, the negative primary current begins to flow directly with the illumination. This starting value is proportional to the intensity of the light used. Immediately however the excitation begins to play a part (the electrons become fixed and form space charges) and the photoelectric current decreases. At relatively great intensities of light this decrease is rapid (Fig. 103*a*) and a constant value is finally reached (at least when the whole crystal between the

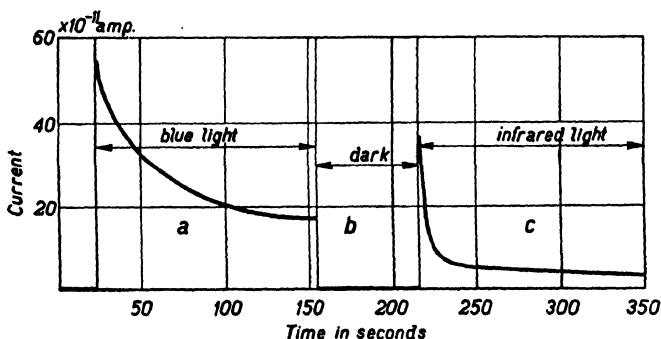


Fig. 103. Photoelectric currents in yellow rock-salt crystals at a temperature of 33° C. and a relatively high intensity of light.

electrodes is illuminated, otherwise the current falls to zero). If now the illumination is interrupted, a very small current continues to flow (Fig. 103*b*, gradual neutralization of the excitation); if one now illuminates with infrared the positive primary current suddenly flows, but with rapidly decreasing intensity (Fig. 103*c*; the electrons are emitted from the excitation centres and finally reach again the previously formed positive charges). At low light intensities the negative primary current begins directly upon illumination with blue light and decreases only very gradually (Fig. 104*a*). If the illumination is now cut off a small current continues to flow in this case also as in Fig. 103*b* (Fig. 104*b*). Infrared illumina-

\* Z. Gyulai, *Z. Phys.* 33, 251 (1925).

tion gives again the rapid neutralization of the excitation (Fig. 104c). At a higher temperature the electrons are more

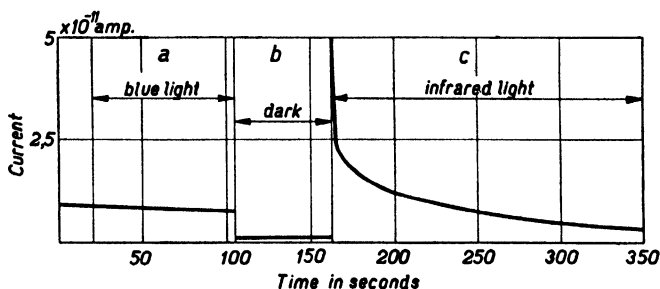


Fig. 104. Photoelectric currents in yellow rock-salt crystals at a temperature of 33° C. and a low intensity of light. Gudden and Pohl.

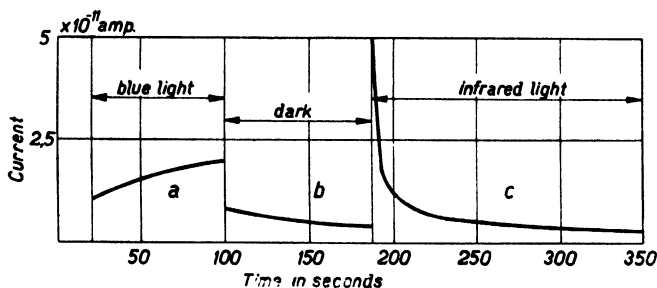


Fig. 105. Photoelectric currents in yellow rock-salt crystals at a temperature of 77° C. and a low intensity of light. Gudden and Pohl.

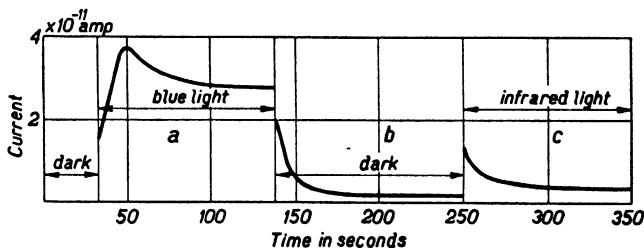


Fig. 106. Photoelectric currents in yellow rock-salt crystals at a temperature of 125° C. and a low intensity of light. Gudden and Pohl.

easily freed from the excitation centres, the photoelectric current therefore increases with the time (Fig. 105a) and then an ever increasing part of the positive primary current flows

simultaneously with the negative primary current. If now the illumination is cut off this positive primary current continues to flow with gradually decreasing intensity (Fig. 105*b*); infrared illumination neutralizes the remainder of the excitation (Fig. 105*c*). The photoelectric conduction current in these and many other cases have been analysed by the very accurate and systematic investigations of Gudden and Pohl.\* At still higher temperatures still less excitation remains (see for example Fig. 106).

Another very important question is that of the nature of the excitation centres. It might be imagined that in this case the electrons neutralize any arbitrary alkali metal ion in the lattice, and make an atom of this ion temporarily.† The electrons are much more easily freed from such an atom than from an atom adsorbed upon an internal surface or upon a defect of the crystal, which is in agreement with the nature of the excitation centres. According to Schröder‡ the excitation centres are sensitive to structure (see § 74) and are thus connected with the action of crystal defects. Now the excitation centres are formed from the colour centres, thus from alkali metal atoms adsorbed at defects of the crystal, while upon their disappearance they pass over into such atoms. Therefore the excitation centres must be sensitive to structure by their very nature, so that it is not necessarily impossible on the basis of the sensitivity to structure of these centres that we are still concerned with neutral atoms in the lattice.

It is, however, at least not improbable that in the excitation centres the electrons have neutralized alkali metal ions, which occur at defects of the crystal. Smekal§ assumes in this connection that in this excitation alkali metal ions are neutralized, which occupy particular places at defects of the crystal structure, for example, ions at corners or edges of internal surfaces. In this way it could be explained why the electrons are so much

\* B. Gudden and R. W. Pohl, *Z. Phys.* **31**, 651 (1925).

† J. H. de Boer and W. de Groot, *Z. Phys.* **83**, 517 (1933).

‡ H. J. Schröder, *Z. Phys.* **76**, 608 (1932).

§ A. Smekal, *Phys. Z.* **33**, 204 (1932).

more easily freed from the excitation centres than from the ordinary internally adsorbed sodium atoms. One may however also ask whether the extra negative charge at the excitation centres is not already sufficient to explain this phenomenon. In the case of the ordinary colour centres provision for electrical neutrality is already made during their formation (§§ 74, 75 and 82). These internally adsorbed atoms exist thus in an environment in which there is no superfluous positive or negative ion. With the excitation centres the case is different; in that case the electron arriving neutralizes an ion of a crystal defect and thereby causes the disappearance of a positive ion at that spot, thus causing the presence of one more negative ion in relation to the positive ions. Under the influence of one extra negative charge, however, the alkali metal atom here formed will lose its electron more easily than an alkali metal atom of the colour centres (cf. also §§ 62 and 65), so that the difference between the excitation centres and the colour centres is explained by this fact.

#### § 78. Bleaching of coloured crystals of the alkali halides.

When the photoelectrically conducting alkali halides are prepared photochemically by illumination with short-wave ultraviolet light (§ 74) or with X-rays, the electrons photoelectrically split off from the internally adsorbed alkali metal atoms can be recaptured by halogen atoms instead of forming excitation centres. Besides the alkali metal atom there is a halogen atom formed in the photochemical colouring of the alkali halides, which halogen atom is also adsorbed upon an internal surface. If now an electron is liberated by irradiation within the absorption band of the internally adsorbed alkali metal atoms, this electron may after having covered a certain distance in the lattice meet such a halogen atom and transform it into a halogen ion. The absorption band of the internally adsorbed atoms, i.e. of the colour centres, decreases in intensity thereby, without the appearance of absorption farther toward the red in its place as was the case in excitation. The capture of electrons by halogen atoms consequently brings about a bleaching of the coloured crystal. This bleaching, which has

been known for a long time,\* is in a certain sense analogous to the bleaching effect known as the Herschel effect in the case of the silver halides in the photographic plate, which consists in the fact that flooding an exposed photographic plate with infrared light before development destroys the latent image.

The electron liberated from the internally adsorbed alkali metal atom does not in this bleaching process join a halogen atom directly adjacent. Hilsch and Pohl† found that the process of bleaching is accompanied by a photoelectric current, whereby the electrons move several tenths of a micron through the lattice, and whereafter they are captured by a halogen atom.‡ The halogen and alkali atoms formed next to each other upon an internal surface by the photochemical colouring will probably not remain next to each other, but will be separated by means of a thermal movement§ (migration along an internal surface). This migration probably remains confined to the internal surface in question, since crystals with small imperfections exhibit a stronger bleaching effect than crystals with coarse imperfections.|| From this fact it may be concluded that the bleaching process is also sensitive to structure (§ 74).¶

Smakula\*\* has examined the relative importance of the processes of excitation and bleaching. Low temperature favours excitation at the cost of bleaching. Synthetic crystals of potassium chloride which were coloured by X-ray radiation, gave upon irradiation with light of a wave-length between 500 and 600m $\mu$  (cf. Fig. 97) at room temperature 100 per cent.

\* E. Goldstein, *Ann. Phys.*, Lpz., **60**, 491 (1897); W. C. Röntgen, *Ann. Phys.*, Lpz., **64**, 1 (1921).

† R. Hilsch and R. W. Pohl, *Z. Phys.* **68**, 721 (1931).

‡ After they have rejoined a halogen atom the electrons are lost for photoelectric conduction; in contrast to excitation bleaching is an irreversible process.

§ A. Smekal, *Phys. Z.* **33**, 204 (1932).

|| H. J. Schröder, *Z. Phys.* **76**, 608 (1932).

¶ Cf. also: M. N. Podaschewsky, *Naturwissenschaften*, **16**, 653 (1928); *Z. Phys.* **50**, 369 (1929); **65**, 799 (1930); A. Smekal, *Naturwissenschaften* **16**, 760 (1928); M. Haberfeld, *S.-B. Akad. Wiss. Wien*, **142**, 135 (1933).

\*\* A. Smakula, *Z. Phys.* **59**, 603 (1930).

bleaching; at  $-186^{\circ}\text{C.}$ , however, they gave 75 per cent. bleaching and 25 per cent. excitation. When natural sodium chloride coloured by means of X-rays was illuminated at room temperature with a wave-length between 440 and  $500\text{m}\mu$ , 15 per cent. of the electrons freed passed to halogen atoms (bleaching) and 85 per cent. to excitation centres; at  $200^{\circ}\text{C.}$ , however, no excitation but only bleaching was found.

## CHAPTER XI

### ELECTRONIC CONDUCTION IN THE LATTICES OF THE ALKALI HALIDES, AND RELATED PHENOMENA

#### § 79. Thermal ionization of adsorbed atoms.

The valence electrons of adsorbed alkali or alkaline earth metals can be freed by the absorption of light and emitted to

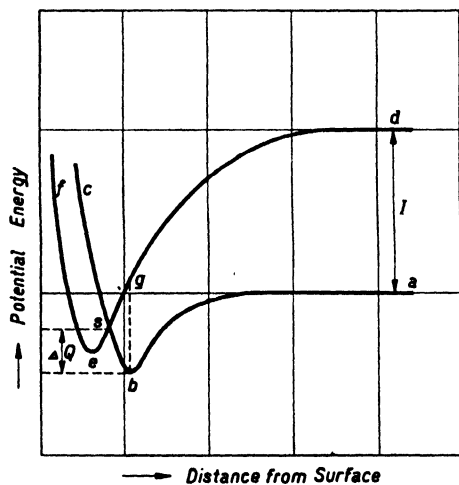


Fig. 107. Potential curves for the adsorption of an atom or an ion on a surface.

the outside (selective photoelectric effect, § 62 and Chap. ix), or within the lattice (photoelectric conduction, § 76). Ionization of these adsorbed atoms may also be brought about thermally in many cases. Let us again examine the potential curves which may be drawn for such a case of adsorption (Fig. 107, cf. also Fig. 78 in § 62). Curve *abc* represents the potential curve for the adsorbed atom, *def* that for the adsorbed ion. We shall consider the case in which the electron is emitted to the outside (for emission in the lattice, cf. § 85); in this case the distance between the energy levels *a* and *d* is equal to the ionization energy of the free, non-adsorbed atom. In the

treatment of the selective photoelectric effect we saw that there is a transition from the lower curve to the higher one, and that the change in energy thereby is represented by the distance from the point *b* to the point *g* vertically above *b* on the curve *def* (Franck-Condon principle). If the temperature of the system, surface + adsorbed atom, is increased the atom acquires vibration energy with respect to the surface. The vibrations are adequately represented by the form of the curve *abc* about the point *b* (§ 53). If now the temperature is raised so high that some of the atoms reach point *s* in their vibrations due to the thermal energy, something special takes place. At such an intersection of potential curves there is a certain probability of a transition from one curve to the other (§ 21, Fig. 25, and § 56). This means that the atom is ionized and the electron emitted.\* Thus we see that for the emission of electrons to the outside a quantity of thermal energy equal to the difference in height  $\Delta Q$  between *s* and *b* is sufficient; the atom is then ionized thermally. If the total number of adsorbed atoms per cm.<sup>2</sup> of surface is equal to  $n_0$ , then the number of atoms *n* which reaches the intersection point *s* will be represented by the Maxwell equation:

$$n = Cn_0 e^{-\frac{\Delta Q}{kT}},$$

where *C* is a proportionality factor. The number of atoms ionized, and thus the number of electrons emitted,  $n_e$ , will be proportional to the above and thus equal to

$$n_e = CC'n_0 e^{-\frac{\Delta Q}{kT}}.$$

The atoms adsorbed on internal surfaces may also be ionized in a similar way by the addition of thermal energy. Since, however, in this case the electrons are emitted in the lattice, the energy necessary cannot be represented directly, because of the fact that only those electrons can be introduced into a lattice whose energy corresponds with definite permitted energy bands of the lattice (§§ 72 and 85). In the case of thermal ionization of internally adsorbed atoms this pheno-

\* J. H. de Boer, *Chem. Weekblad*, 29, 34 (1932); J. H. de Boer and M. C. Teves, *Z. Phys.* 83, 521 (1933).



menon thus leads to a thermal electronic conduction in the lattices.

We shall return later (Chap. XIV) to the external emission of such thermally liberated electrons, and shall in the following sections first discuss this thermal conduction.

**§ 80. The splitting off of electrons from internally adsorbed atoms by heating.**

In § 77 we saw that the electrons can be freed from the excitation centres by the taking up of thermal energy (already appreciable at ordinary temperatures, and quite strong under application of heat). We must however also expect something similar in the case of the colour centres, i.e. of the ordinary internally adsorbed atoms. In some excellent experiments by Stasiw\* which were carried out in Pohl's laboratory in Göttingen this thermal, internal emission of electrons has actually been found and demonstrated in a very convincing manner. A crystal of potassium chloride in which potassium atoms are introduced (in Stasiw's experiments there was approximately one internally adsorbed potassium atom for every  $10^5$  molecules of potassium chloride) by additive coloration (heating in potassium vapour) is heated to above  $350^\circ\text{C}$ . The crystal is then blue: at  $400^\circ\text{C}$ . for example the maximum of the absorption band of the colour centres lies at  $605\text{ m}\mu$ . On both sides of the crystal platinum wire electrodes are fused in, so that an electric field can be applied to the crystal. The passage of a current can be immediately measured, and it falls off with the time (Fig. 108), in order finally to become constant. At the same time one sees that the blue colour is displaced in the field toward the anode, that is to say, the colour disappears at the cathode side and simultaneously with the decrease of the current the non-coloured portion becomes larger, and the colour centres apparently disappear into the anode. The boundary between the coloured and the non-coloured portion remains quite sharp. At the moment when the last of the colour disappears into the anode the current becomes constant. This final constant current is electrolytic in

\* O. Stasiw, *Nachr. Ges. Wiss. Göttingen*, p. 261 (1932).

nature. If the tension is reversed when only half of the colour has disappeared, the blue zone which remained moves as a whole in the opposite direction. The velocity is high: at a tension of about 1000 volts and with a crystal about 1 cm. thick, the whole crystal is decoloured in about 6 seconds at 555° C.

There is a relation between the quantity of electricity in ampere seconds, represented by the shaded area in Fig. 108, and the disappearance of the colour centres. If this quantity of electricity is divided by the absolute charge of an electron

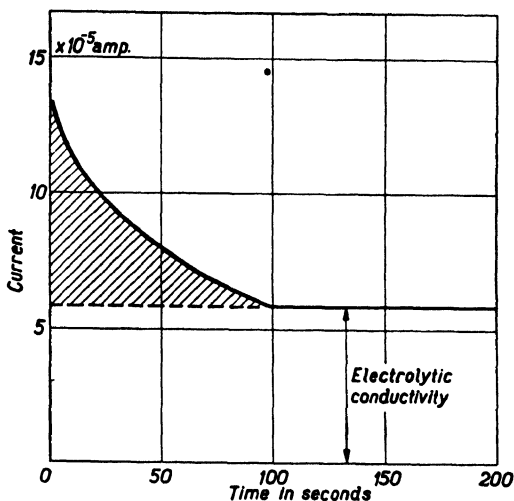


Fig. 108. In an electric field the potassium atoms adsorbed on internal surfaces in potassium chloride move to the anode (467° C.). O. Stasiw, *Nachr. Ges. Wiss. Göttingen* (1932).

( $1.59 \times 10^{-19}$  ampere second) the number of internally adsorbed potassium atoms is obtained. This number may also be calculated optically from the height and breadth of the absorption band before the decoloration\*. Stasiw showed that both electrical and optical methods lead to the same number of internally adsorbed potassium atoms, which proves that one charge disappears for every potassium atom which was present.†

\* A. Smakula, *Z. Phys.* **63**, 762 (1930).

† Footnote added to proof: Cf. E. Mollwo and W. Roos, *Nachr. Ges. Wiss. Göttingen*, Neue Folge, **1**, 107 (1934).

The internally adsorbed potassium atoms apparently move toward the anode in the electric field, and with velocities which indicate that the moving particles are actually electrons. The explanation of this phenomenon is the following. An electron is freed thermally from an internally adsorbed potassium atom in the crystal, and moves through the lattice until, after it has covered a certain distance, it neutralizes a potassium ion on an internal surface to form once more an internally adsorbed potassium atom. The first potassium atom has thus become an ion and thereby no longer a colour centre, while the potassium ion neutralized has become an atom and thereby a colour centre. It appears as if the colour centres were displaced, whereas only electrons move, namely those which are emitted in the lattice.

In the experiment described above the emitted electrons disappear from the lattice without their being supplemented by electrons from the cathode. If the contact between cathode and crystal is very good this supplementation takes place\* and one can no longer perceive visually that anything is taking place, since no decoloration occurs; one measures only the passage of an electric current. A relatively poor contact which allows no supplementation of electrons is thus the condition for the visual observation of the electronic conduction. In this case the positive potassium ions remaining behind are removed by the electrolytic conduction.

### § 81. Electrolytic and electronic conduction in the alkali halides.

If there is no supplementation of electrons from the cathode, the electronic conduction is closely connected with the electrolytic conduction. Electrolytic conduction increases very rapidly with the temperature,† according to a power of  $e$ , because in this case energy must be supplied by thermal agitation to free the ion. The following formula is valid here:

$$\kappa = Ce^{-\frac{Q}{RT}},$$

\* O. Stasiw, *Nachr. Ges. Wiss. Göttingen*, p. 387 (1933).

† Cf. C. Tubandt, *Handbuch. der Experimentalphysik*, 12, 1, pp. 384 ff., Leipzig (1932).

where  $\kappa$  is the electrolytic conductivity and  $Q$  is the energy, necessary to free the ion.\* If the logarithm of the conductivity is plotted against  $\frac{1}{T}$ , a straight line is obtained. Lehfeldt† showed that the alkali halides in the form of pieces of a single crystal, at high temperatures up to their melting points, all exhibit electrolytic conduction, which can be considered a

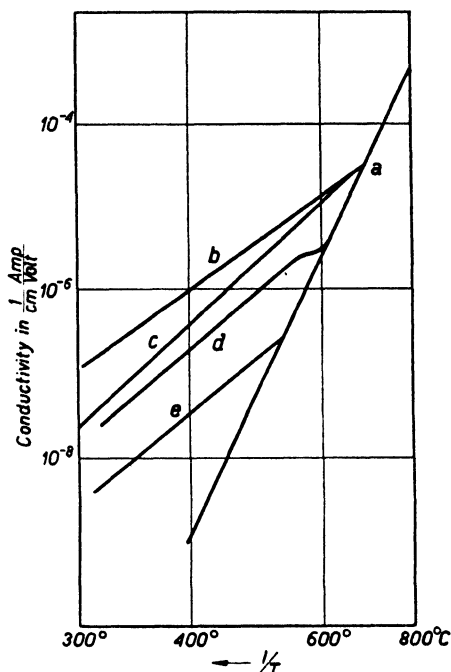


Fig. 109. Electrolytic conductivity of a KCl crystal: *a*, real conductivity of material; *b*, *c*, *d* and *e*, conductivity due to crystal imperfections and impurities. W. Lehfeldt, *Z. Phys.* **85**, 723 (1933).

property of the substance itself, and thus to a high degree insensitive to structure. At lower temperatures, however, an electrolytic conduction dominates which is connected much more with foreign components and places of disturbance and is thus typically sensitive to structure (Fig. 109). This electrolytic conduction which is sensitive to structure (in German

\* E. Rasch and F. W. Hinrichsen, *Z. Elektrochem.* **14**, 41 (1908); C. Tubandt, *loc. cit.* pp. 435 ff.

† W. Lehfeldt, *Z. Phys.* **85**, 717 (1933).

“Störleitung”) is in general greater the more defects there exist in the crystal. Stasiw\* examined the velocity with which the region of colour centres was displaced at various temperatures for several alkali halides (Fig. 110). The velocity at which these colour centres are displaced (at which the electrons move) is proportional to the field strength, since the average distance covered by the electron between the point where it was emitted and the point where it was recaptured is proportional to the field strength (§ 76). Further the velocity increases very strongly with the temperature, which must be ascribed to the circumstance that the number of electrons emitted per unit time, and which begin to move in the lattice, increases as a power of  $e$  upon increase of temperature (§ 79). The velocity which is observed is not the velocity with which the electrons really move when they make a jump within the lattice, but is rather the velocity with which the cloud of electrons is displaced. Stasiw now showed that, in the region where the electrolytic conduction is insensitive to structure, the electronic conduction in the case indicated in Fig. 110 may also be represented by a straight line, if the logarithm of the velocity of displacement is plotted against  $\frac{1}{T}$ . In the

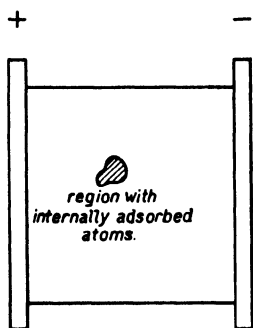


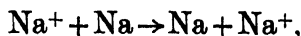
Fig. 110. A crystal of an alkali halide possessing a region in which there are internally adsorbed atoms, placed in an electric field.

region of the “Störleitung”, however, the electronic conduction begins to become irregular; the region in which there are colour centres becomes broader and maximum and minimum values of the velocity may be measured (Fig. 111 *a* and *b*).

If however a crystal is provided throughout with colour centres, and a good contact with the cathode is also provided so that electrons may be supplied from the cathode, the electronic conduction is no longer dominated by the electrolytic conduction. The electronic conduction may then exceed

\* O. Stasiw, *Nachr. Ges. Wiss. Göttingen*, p. 387 (1933).

by far the electrolytic, and may be several powers of ten higher. The alkali halide crystal has then become an electronic conductor without an electrolytic conduction being necessary to maintain the electronic one. The electrons move from one internally adsorbed atom to an ion on an internal surface, transforming this ion into an internally adsorbed atom and so on; the conduction may be represented by the following:



or more generally  $\text{Me}^+ + \text{Me} \rightarrow \text{Me} + \text{Me}^+$ ,

where Me indicates an internally adsorbed atom.

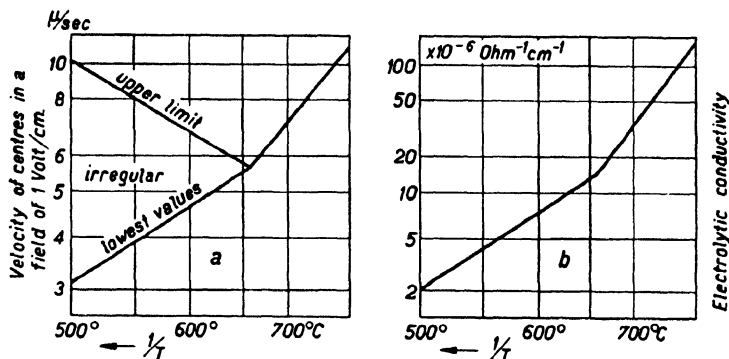


Fig. 111. *a*: Velocity of colour centres in an electric field (K in KCl). *b*: Electrolytic conductivity of the same crystal. O. Stasiw, *Nachr. Ges. Wiss. Göttingen* (1933).

One can also maintain stationary electronic currents photoelectrically, which are several powers of ten greater than the electrolytic conduction. To name only one example,\* a piece of yellow rock-salt gave an electrolytic dark current of  $2 \times 10^{-11}$  ampere at about  $140^\circ \text{C}$ . Upon illumination (with the full light of a tungsten lamp, i.e. not only with blue but also red and infrared, see § 77) a current of  $450 \times 10^{-11}$  ampere was obtained. The phenomenon of excitation† (§ 77) plays an important part under this strong illumination in spite of the relatively high temperature, and therefore the photocurrent decreases immediately; a constant value of  $200 \times 10^{-11}$  ampere is nevertheless obtained. With this stationary current of

\* R. Hilsch and R. W. Pohl, *Z. Phys.* **87**, 78 (1933).

† Cf. also R. W. Pohl, *Phys. Z.* **35**, 107 (1934).

$200 \times 10^{-11}$  ampere, which is 100 times greater than the electrolytic current, there is an equilibrium between the number of electrons liberated by the light and the number of electrons supplied not only out of the electrode but also out of the excitation centres (photoelectrically as well as thermally). The excitation causes an electric polarization in the crystal; if the tension is interrupted after the illumination has ceased and if the crystal is then short circuited and again illuminated, a rapidly decreasing current flows in the opposite direction. If one waits for some time before short circuiting the crystal and again illuminating it, then the polarization is already neutralized by the thermal emission from the excitation centres. The electrolytic conduction also opposes the polarization; at higher temperatures (with NaCl at about  $200^{\circ}\text{C.}$ ), if the photocurrent is of the same order of magnitude as the electrolytic current, polarization is no longer observed.

The great difference between the electronic conduction in the lattices of the alkali halides and that in the metals lies in the fact that the electrons are bound in the former case. In the *metals* the conduction electrons are not bound and move about without resistance at extremely low temperatures (superconduction), at higher temperatures the electrons lose the energy which they continually take up from the electric field by reciprocal action with the positive ions. The agitation of the positive ions due to temperature opposes the passage of the electrons, which explains why the conductivity of metals becomes smaller at higher temperatures. Defects of the lattice, foreign atoms, internal surfaces and impurities act in the same direction, and the conductivity of metals is very materially decreased, due to these causes. Thus here again there is a parallelism between the influence of an increase of temperature and the influence of disturbance places in the lattice.

In the *salts* provided with internally adsorbed alkali metal atoms the number of electrons available for electronic conduction is much smaller than in metals (it is at the most equal to the number of colour centres). To produce conduction these electrons must first be liberated by thermal energy. The agitation of the ions in the lattice due to temperature as well

as crystal imperfections oppose the conduction in this case also; however, their influence upon the dependence of the conduction on temperature is completely dominated by the increase experienced by the conductivity due to the liberation of so many more electrons per unit time at higher temperatures.

Since in metals the electrons are not bound to definite places, they cannot be liberated by light energy in order to move in the lattice as in the alkali halides; therefore in the metals no photoelectric conduction can be observed.\*

That the crystal imperfections as such oppose the electronic conduction, is shown very well from the fact that with equal numbers of colour centres the photoelectric conduction is less according as there are more imperfections in the crystal. If, however, there are more places of disturbance, then more colour centres may be introduced and the photoelectric conduction consequently becomes better.

Places of disturbance favour in addition the electrolytic conduction, at least in the region of the "Störleitung".†

## § 82. The mechanism of additive coloration.

We can now also understand the mechanism of the additive coloration, i.e. of the so-called diffusion of alkali metal atoms into their lattices. In § 75 we mentioned that it seemed quite clear from Rexer's work that there is no question here of ordinary diffusion. We are here actually concerned with a penetration of electrons into the lattice.‡ In the heating of the crystals in the vapour of alkali metals alkali metal atoms are adsorbed on the surface of the crystal and probably also on the surfaces of cracks (compare the swelling in § 60). These atoms may lose their electron thermally and emit it into the

\* In very thin metallic films the electrons are no longer free; the conductivity decreases less rapidly with increasing temperature, or it may even increase. In the case of such thin metallic films one should be able to free electrons in the lattice by illumination, and the films should therefore exhibit photoelectric conduction. R. Schulze (*Phys. Z.* **34**, 381 (1933)) has actually discovered a photoelectric conduction with thin gold and magnesium films.

† Cf. G. v. Hevesy, *Z. Phys.* **36**, 481 (1926); *Z. Elektrochem.* **34**, 463 (1928); A. Smekal, *Z. techn. Phys.* **8**, 561 (1927).

‡ O. Stasiw, *Nachr. Ges. Wiss. Göttingen*, p. 261 (1932).



lattice; within the lattice the intruding electrons neutralize alkali metal ions of internal surfaces to give internally adsorbed atoms and they may continue in the same way, moving from ion to ion (on internal surfaces) and neutralizing these ions. At the temperature at which additive coloration takes place the space charges formed (the negative electrons have diffused to the inside, the positive ions remain behind) are neutralized by the electrolytic movement of the alkali metal ions, which thus follow the electron in the lattice. This last statement must be conceived in the following way: after several electrons have already diffused to the inside, several alkali metal ions in the lattice move in the same direction in order to neutralize the space charge, hereupon several more alkali metal ions which were somewhat closer to the surface follow, and again several more ions which diffuse from the surface to the inside. If the process of penetration is interrupted the space charges are not completely neutralized, and before the crystal has cooled off the colour centres (electrons) which have advanced the most are drawn back again.\*

As was stated in § 75 the properties of the colour centres formed in the lattice in this manner, and especially the positions of their absorption bands, are identical with those of colour centres introduced photochemically. Under special circumstances other absorption bands may be obtained. The other absorption bands may be ascribed in part to particles of colloidal dimensions—this will be discussed in § 84—and in part to causes which have no colloidal nature. Thus Rexer† obtained a formation of colloidal particles by the “diffusion” of sodium in sodium chloride which had undergone a temperature treatment, and the colloidal particles broke up again partially at a higher temperature, to give after cooling colour centres which were not of a colloidal nature and which showed an absorption band at  $440\text{ m}\mu$  (instead of at  $465\text{ m}\mu$ ). These new colour centres are remarkably stable and lose their electrons at high temperatures much less easily than the ordinary colour centres. In the case of natural blue rock-salt

\* E. Rexer, *Z. Phys.* **70**, 159 (1931); **76**, 735 (1932).

† E. Rexer, *Z. Phys.* **86**, 1 (1933).

(blue rock-salt contains colloidal particles) maxima of the light absorption can also be obtained which lie at shorter wavelengths than that of the normal colour centres. A similar phenomenon takes place when foreign atoms such as atoms of lead, bismuth or gallium have diffused into sodium chloride.\* Miss Blau† also obtains entirely different absorption bands lying more toward the ultraviolet in the case of alkali halides after the "diffusion" of alkali metals into the crystals in which there are small amounts of silver, copper or thallium ions. She has, however, shown that these bands must probably be ascribed to atoms of silver, copper or thallium respectively, which are freed from their ions in the "diffusion" of the alkali metal into the crystal.

If a crystal of an alkali halide is heated in the vapour of another alkali metal, only those colour centres are formed which correspond to the metal present in the compound. For example, sodium chloride after being heated in potassium vapour gives only the absorption band at  $465\text{ m}\mu$  which is to be ascribed to internally adsorbed sodium.‡ On the basis of the mechanism described in this section this is quite clear. The electrons penetrate into the lattice and there form internally adsorbed sodium atoms. The potassium ions also penetrate superficially into the sodium chloride by electrolysis, but deeper in the crystal a displacement of sodium ions makes provision for electrical neutrality.

### § 83. The formation of *U* centres in additive coloration.

In the process of additive coloration other quite different absorption bands may be created. §

When, after additive coloration, the crystal is heated to a high temperature ( $50^\circ$  below its melting point) without the presence of alkali metal vapour, colour centres evaporate out

\* E. Rexer, *Naturwissenschaften*, **21**, 332 (1933).

† M. Blau, *Nachr. Ges. Wiss. Göttingen*, p. 401 (1933).

‡ F. Giesel, *Ber. dtsh. chem. Ges.* **30**, 156 (1897); H. Siedentopf, *Phys. Z.* **6**, 855 (1905); Z. Gyulai, *Z. Phys.* **37**, 889 (1926); E. Rexer, *Z. Phys.* **70**, 182 (1931).

§ R. Hilsch and R. W. Pohl, *Nachr. Ges. Wiss. Göttingen*, pp. 322, 406 (1933).

again, that is to say, electrons move toward the outside, positive ions follow and it can be proved that alkali metal atoms have evaporated. During this process an intense emission of light from the crystal may be observed. The crystal then becomes quite colourless and no longer emits light. If it is now cooled to room temperature apparently all internally adsorbed atoms have disappeared. It turns out, however, that instead of the absorption band of the colour centres (band *F*—from the

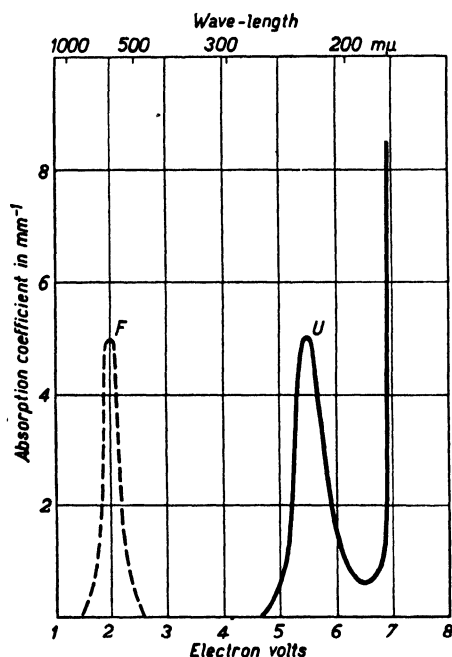


Fig. 112. *F* and *U* bands from a RbCl crystal. R. Hilsch and R. W. Pohl, *Nachr. Ges. Wiss. Göttingen*, p. 322 (1933).

German word “Farbzentren”—in Fig. 112) a new absorption band at a shorter wave-length (band *U*—from ultraviolet) has been created, which new band is superposed upon the long-wave extension of the ultraviolet absorption of the compound itself. What has occurred in this process is not yet entirely clear, in any case centres are formed—the *U* centres—which contain relatively tightly bound electrons. Table X gives the maxima of the absorption bands of the *U* centres for several alkali halides.

Table X. *Maxima of the absorption bands of U centres for several alkali halides*

Salt	Maximum of <i>U</i> band in $m\mu$	Energy corresponding to maxima in electron volts	Ionization energy of alkali metal in electron volts
NaCl	192	6.42	5.12
NaBr	210	5.87	5.12
KCl	214	5.76	4.32
KBr	228	5.42	4.32
KI	244	5.05	4.32
RbCl	230	5.37	4.16
RbBr	242	5.10	4.16

Absorption of light within the *U* band leads to the disappearance of this band, while at the same time the *F* band is built up. Thus a colourless crystal of potassium bromide, which has no ordinary colour centres (*F* bands) but which does have *U* centres, is coloured blue by illumination with light of  $226 m\mu$  (maximum of the *U* band,  $228 m\mu$ ), since colour centres are formed (maximum at  $630 m\mu$ ). At the beginning of the illumination—at least at room temperature—one colour centre of the *F* band is formed for every quantum of light absorbed within the *U* band. Just as many *U* centres disappear under the illumination as colour centres of the *F* band are formed. The shaded *F* band in Fig. 113 was formed while the shaded portion of the *U* band was disappearing.

Conversely, the *F* bands may also be transformed into *U* bands. This can be done optically by irradiation within the *F* band, although in this way only a very few (10 per cent. at the most) of the *U* centres are re-created. The transformation of *F* centres into *U* centres proceeds better by careful heating of the crystal. During this thermal re-creation of the *U* centres the crystals glow with a bluish-violet light. This same light is also obtained if the crystal which has *U* centres is illuminated with light which is absorbed by the *U* centres. In the building up of the *F* centres from the *U* centres part of the *F* centres appear to have only a short life and to go over again into *U* centres with radiation of phosphorescent light. This

phosphorescent light consists of a number of narrow equidistant emission bands.

The dependence on temperature of the position of the  $U$  bands is very similar to that of the  $F$  bands (§ 76), which distinguishes these bands also from those of colloidal particles which are much less dependent on temperature. The very strong bond of an electron in a  $U$  centre makes understandable the failure to split off an electron thermally; the  $U$  centres cannot therefore be displaced in an electric field.

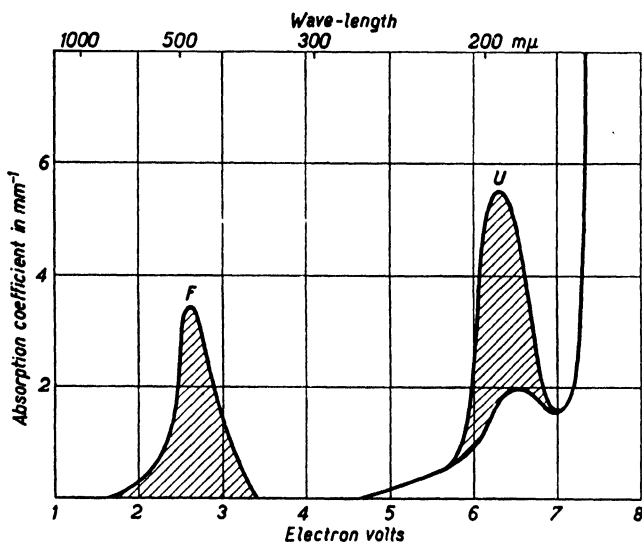


Fig. 113. After irradiation with ultraviolet light, the shaded part of the  $U$  band has disappeared and the  $F$  band is built up (NaCl). R. Hilsch and R. W. Pohl, *Nachr. Ges. Wiss. Göttingen*, p. 324 (1933).

If, however, a crystal with  $U$  centres is heated in an electric field, and afterwards illuminated within the absorption band of the  $U$  centres, the  $U$  centres immediately form  $F$  centres, which are displaced in the electric field. In this method of making the  $U$  centres disappear electrically in the form of  $F$  centres, the quantity of charge which disappears (shaded portion in Fig. 114) is equal to the number of  $U$  centres which was determined optically. After the  $U$  centres have disappeared in the above-described manner, no more  $U$  centres can be obtained by allowing electrons to penetrate into the crystal,

only  $F$  centres are formed. The places of the  $U$  centres seem to be irrevocably wiped out by the electrolytic current.

We have as yet too little knowledge to be able to discuss the nature of the  $U$  centres with certainty. Hilsch and Pohl\* imagine the mechanism of additive coloration to be as follows. Electrons penetrate into the crystal. In order to compensate for the excess negative charge thereby formed, neutralization must be provided for electrolytically. This may take place by the diffusion of positive ions in and into the lattice after the

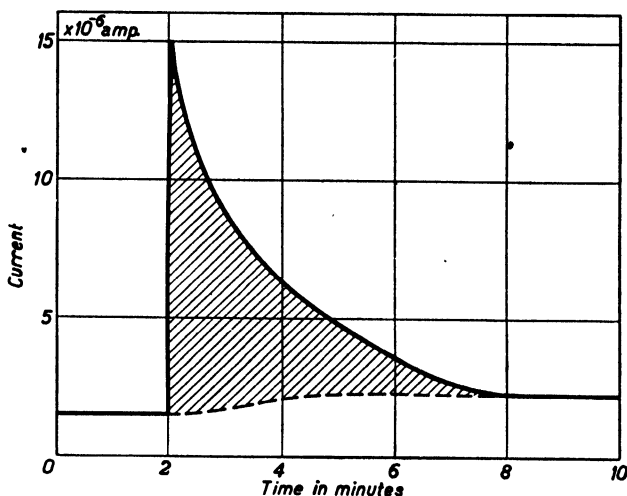


Fig. 114. In a KBr crystal at 375° C., the  $U$  centres move away to the anode in the form of  $F$  centres during irradiation in the  $U$  band. R. Hilsch and R. W. Pohl, *Nachr. Ges. Wiss. Göttingen*, p. 409 (1933).

electrons (§ 82); thereby only  $F$  centres are formed. It may also be brought about by the diffusion of negative ions out of the lattice to the outside; thereby  $U$  centres are formed. They consider the  $U$  centres to be electrons which occupy the place in the lattice of a halogen ion which has disappeared. An  $F$  centre (colour centre) is according to their conception a superfluous electron present in the lattice, in whose neighbourhood—at least if it has been formed by additive coloration—a positive ion is found at a place of disturbance of the crystal. As has been repeatedly explained above, we prefer a somewhat different view, namely, we consider the colour centres to be

\* R. Hilsch and R. W. Pohl, *loc. cit.*

internally adsorbed atoms. These internally adsorbed atoms have, thanks to their adsorption, a lowered ionization potential (§ 79). Not only in the photochemical manner of formation, but also in additive coloration is an alkali metal ion (on an internal surface) neutralized, which ion is bound in a natural way to at least one negative halogen ion, so that just as in the adsorption on external surfaces discussed in §§ 62 and 65 the ionization potential of the atom formed will be lower than that of a free atom. If neutrality in the crystal in the

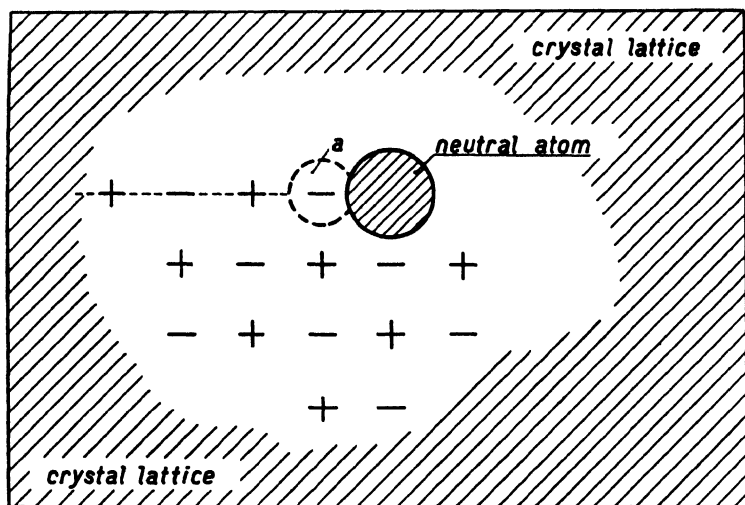


Fig. 115. Diagram of an atom adsorbed on an internal surface.

case of additive coloration is obtained by the diffusion of alkali metal ions in and into the crystals, then this has no influence upon the bond of the internally adsorbed atom which is favourable for ionization.\* The case is quite different, however, if a negative halogen ion is actually removed to bring about neutralization after the transformation of a positive alkali metal ion on an internal surface into an atom. In general the fact that such a negative ion (ion *a* in Fig. 115, for example) is moved away will make the ionization of the adsorbed atom more difficult; as a result of its removal the atom is adsorbed upon more positive ions (Fig. 116), so that the photoionization

\* If this neutralization did not take place, we should be dealing with an excitation centre, see § 77.

will take place only at much shorter wave-lengths. We saw in § 70 that the photoionization band of alkali metal atoms which are adsorbed next to positive ions lies at very short wave-lengths, since the minimum of the potential curve for the atom is quite deep and that of the potential curve for the ion is much less deep (in ionization a positive ion is formed next to a positive ion already present). We have also seen in § 70 that in such cases the photoionization often occurs at still shorter wave-lengths than in the gaseous state. Here again the  $U$  band lies at shorter wave-lengths than the ionization limit for

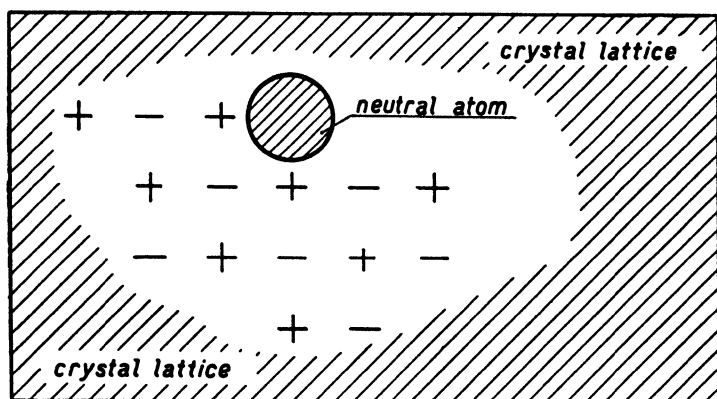


Fig. 116. Diagram giving a possible explanation of a  $U$  centre.

gaseous atoms, and thus the  $h\nu$  value of the  $U$  band is greater than the ionization energy of the atom under consideration (see Table X).

Whether or not the  $U$  bands must actually be ascribed to alkali metal atoms which are adsorbed on positive portions of internal surfaces, further research must show. It is of course also possible that foreign atoms with a certain electron affinity play a part here, as Hilsch and Pohl\* expressly argue.†

#### § 84. Coagulation to form centres of colloidal dimensions.

When electrons are liberated from the internally adsorbed alkali metal atoms either photoelectrically or thermally, these

\* R. Hilsch and R. W. Pohl, *Nachr. Ges. Wiss. Göttingen*, p. 416 (1933).

† For some new experiments on  $U$  centres, cf. A.-D. v. Lüpke, *Ann. Phys.*, Lpz., 21, 1 (1934).



electrons pass a certain distance through the lattice and are then recaptured in some way. In this process excitation centres may be formed (§§ 77 and 81) or a bleaching is possible of crystals which were originally photochemically coloured. It is however also possible that these electrons neutralize alkali metal ions to give atoms, which lie next to atoms already present. In that case larger atom complexes may be formed in the lattice which begin to take on colloidal dimensions. The atomic dispersion thus passes over into a colloidal dispersion, and coagulation takes place by means of movement of electrons. This coagulation, as is immediately clear from the above, can take place photoelectrically\* or thermally.† Simultaneous illumination and heating leads especially rapidly to colloid formation.\*

Additively coloured crystals are especially suitable for coagulation to form colloidal particles. In the photochemically coloured crystals the bleaching is the main occurrence, that is to say the recapture of the freed electrons by halogen atoms. Coagulation may also be obtained photoelectrically along with the bleaching;‡ thermally, however, the bleaching phenomena remains the chief concern. Thus Mollwo† found that photochemically coloured yellow rock-salt was decoloured by heating to between 250 and 300° C. In the additively coloured crystals coagulation begins in the same range. This process of coagulation can be followed optically since the colloids formed have quite different absorption bands lying more toward the red than the bands of the atomic centres. Mollwo passed light of a wave-length of 465 m $\mu$  (maximum of the absorption band for the atomic dispersion of sodium at room temperature) through his yellow sodium chloride crystal. At 250–300° C. the crystal became practically transparent for this light (Fig. 117). Above 450° C. the crystal begins again to absorb blue light—at this point the colloidal particles fall apart again to atoms. Above 550° C. one is again exclusively concerned with atomic centres,

\* M. Savostianowa, *Nature*, London, **126**, 399 (1930); *Z. Phys.* **64**, 262 (1930); E. Rexer, *Phys. Z.* **33**, 202 (1932); *Z. Phys.* **76**, 735 (1932).

† E. Mollwo, *Nachr. Ges. Wiss. Göttingen*, p. 254 (1932).

‡ M. Savostianowa, *loc. cit.*

at still higher temperatures the evaporation of sodium becomes appreciable.

If the crystal is suddenly cooled from  $550^{\circ}\text{C.}$  to room temperature, the atomic dispersion is retained; if it is gradually cooled, colloidal centres are obtained. At room temperature and other temperatures up to  $450^{\circ}\text{C.}$  the colloidal centres represent the most stable distribution of the sodium, at higher temperatures the atomic centres are stable.

The colloidal centres are highly sensitive to structure. Rexer\* made use of this fact in order to study ultra-micro-

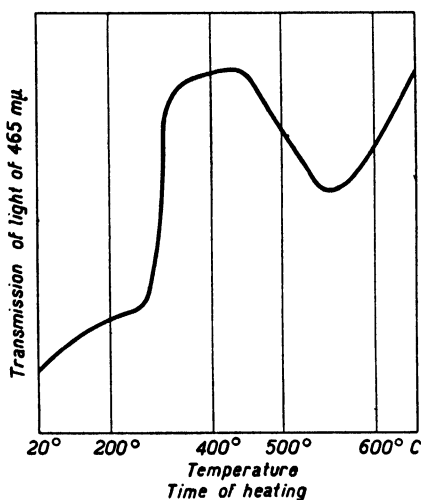


Fig. 117. Transmission of blue light ( $465\text{ m}\mu$ ) through a yellow rock-salt crystal, at various temperatures. E. Mollwo, *Nachr. Ges. Wiss. Göttingen*, p. 254 (1932).

scopically changes in the lattice which are due to the previous history or are introduced by a heat treatment or plastic deformation.

When a sodium chloride crystal which has had no special heat treatment is coloured additively by heating it to  $500\text{--}600^{\circ}\text{C.}$  in sodium vapour, no ultramicros are observed during the process of diffusion; the crystal is coloured a homogeneous brown and all the sodium is atomically dispersed (see also Fig. 117). Upon cooling, ultramicros appear and coagulation takes place. It is, however, quite different when the sodium chloride

\* E. Rexer, *Z. Phys.* **76**, 735 (1932).

crystal has been submitted to a heat treatment above  $600^{\circ}\text{C}$ . before the experiment, and the substance is then homogenized. Upon subsequent heating in sodium vapour coagulation already takes place at the "diffusion temperature", and many very small red ultramicros are formed. These ultramicros are actually much more stable than those with substances which have not previously been homogenized at a high temperature. With untreated sodium chloride a "freezing in" of the atomic distribution is obtained after the penetration of sodium into the crystal and the rapid cooling, as was mentioned above, and the crystal is then yellow. Heating to above  $200^{\circ}\text{C}$ . gives coagulation, small colloidal particles are formed, and the crystal becomes red-violet; heating to higher temperatures gives larger colloidal particles and the crystal turns blue. At still higher temperatures ( $400^{\circ}\text{C}$ . and higher) the colloidal particles, as we saw above, fall apart to give again an atomic distribution, and the ultramicros disappear. The sodium ultramicros which are arranged along coarse internal cracks disappear last in this process. In the case of sodium chloride which has previously been homogenized at above  $600^{\circ}\text{C}$ ., the phenomena are quite different. At all temperatures below  $400^{\circ}\text{C}$ . the small very stable ultramicros exist, above  $450^{\circ}\text{C}$ . their number begins to decrease, but some are still present at  $600^{\circ}\text{C}$ . Atomic dispersion giving the well-known maximum at  $465\text{ m}\mu$  does not occur, although there is a band at  $440\text{ m}\mu$  (§ 82). Upon plastic deformation sodium chloride exhibits gliding phenomena along dodecahedral planes. The ultramicros arrange themselves along these planes in the colloidal dispersion so that the consequent formation of stripes is extraordinarily clearly visible.

Not only by ultramicroscopic observation but also from the absorption spectra may the colloidal dispersion be recognized.\* In Fig. 118 not only the absorption band of the atomic dispersion of sodium in sodium chloride is represented, but also an absorption band of a colloid having very small particles, and one of a colloid with much larger particles. In contrast to the absorption bands of the colour centres of the

\* E. Mollwo, *Nachr. Ges. Wiss. Göttingen*, p. 254 (1932); M. Savostianowa, *Z. Phys.* **64**, 262 (1930); E. Rexer, *Z. Phys.* **86**, 1 (1933).

atomic dispersion, the absorption bands of the colloidal dispersion hardly change at all with the temperature. In natural blue rock-salt still other bands exist lying more toward shorter wave-lengths.\*

In the transition from an atomic dispersion to a colloidal one or the reverse, the total quantity of alkali metal in the crystal remains naturally unchanged as long as no evaporation out of the lattice takes place; this can be proved optically.†

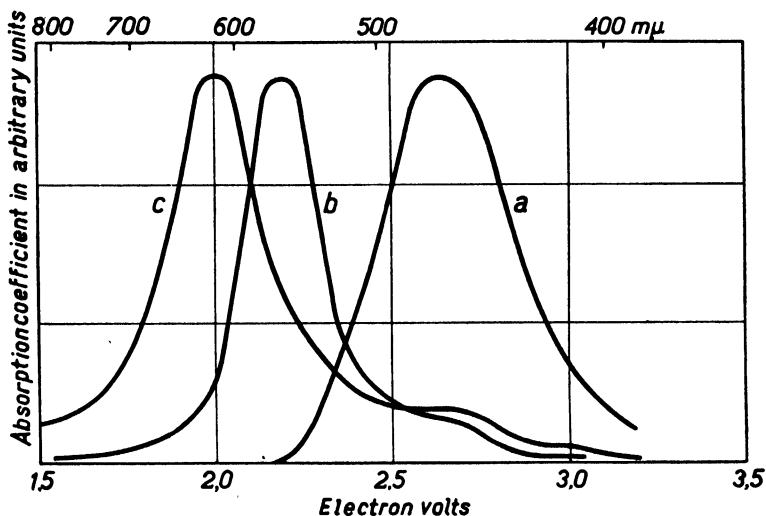


Fig. 118. Absorption spectra of (a) sodium atoms in sodium chloride at 20° C.; (b) small colloid particles of sodium in sodium chloride, as prepared at 350° C.; (c) larger colloid particles of sodium in sodium chloride, as prepared at 450° C. E. Mollwo, *Nachr. Ges. Wiss. Göttingen*, p. 254 (1932).

The colloidal particles as such may take the part of sources of electrons in the case of a thermal or photoelectric emission within the lattice. The thermal liberation of electrons has already been mentioned; the falling apart of the colloidal particles at higher temperatures (above 450° C.) begins by the liberation of electrons. Electrons may also be detached photoelectrically and they then contribute to the conduc-

\* Z. Gyulai, *Z. Phys.* **37**, 889 (1926); R. Hilsch and R. Ottmer, *Z. Phys.* **39**, 644 (1926).

† E. Miescher, *Nachr. Ges. Wiss. Göttingen*, p. 329 (1933).

tion in the lattice.\* Gyulai† has investigated the spectral distribution of the photoelectric conduction for natural blue rock-salt (Fig. 119). In contrast to what we observed in the atomic dispersion (§ 76, Fig. 100) this spectral distribution is very different from the absorption spectrum. We are here no longer concerned with an ionization band of adsorbed atoms; in the emission of electrons it is rather the conduction electrons of the colloidal particles, consisting of very small sodium crystals, which are emitted. The difference between the atomic and the colloidal dispersion is analogous to what we have seen in §§ 62 and 65 in the adsorption of caesium on

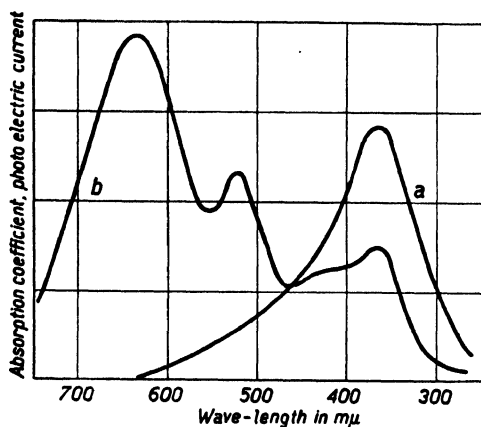


Fig. 119. Spectral distribution of photoelectric current (a) and absorption spectrum (b) of natural blue rock-salt.

external surfaces; in the external adsorption also as soon as small regions are formed where there can be a question of conduction electrons, the photoelectric emission decreases and the spectral distribution no longer corresponds to the absorption spectrum. In both cases, i.e. that of external adsorption‡ (§ 62, Fig. 77), and the case under consideration of internal adsorption, an additional strong absorption of light is found at longer wave-lengths, which does not lead to the emission of electrons.

\* R. Hilsch and R. W. Pohl, *Z. Phys.* **87**, 84 (1933).

† Z. Gyulai, *Z. Phys.* **35**, 411 (1926).

‡ J. H. de Boer, J. F. H. Custers and C. J. Dippel, *Physica*, **1**, 935 (1934).

### § 85. Energy zones in the alkali halides.

We have already mentioned several times that in a lattice like that of an alkali halide electrons can exist only in certain energy ranges (§§ 72 and 79). In an individual atom electrons can only exist in certain states of energy, these energy levels are however quite discrete, the transition from one level to the other leading to sharp absorption or emission lines (§ 11). In a lattice taken as a whole, we must also imagine that electrons can only exist in certain energy states; we have, however, no longer any sharply defined energy levels, but energy zones in which electrons can exist, which zones are separated by regions in which electrons cannot occur.\*

When an electron is emitted from an internally adsorbed alkali metal atom in the lattice, this electron must be brought into one of the permitted energy bands of the lattice. Not only is there a minimum amount of energy which allows this transition to take place (red threshold), as in the emission to the outside, but there will also be a maximum amount of energy. While in the emission of electrons to the outside there is a red threshold, but no upper energy limit, since the electrons—theoretically at least—can take up any arbitrary amounts of kinetic energy, in the case of emission *within* the lattice a red as well as a violet limit may be expected. In § 69 we saw that in the photochemical colouring process some atoms are also adsorbed on the outside surface of thin films of alkali halides. Upon illumination these atoms emit their electrons to the outside and Fleischmann† found that the spectral distribution of the photoemission is such that emission starts at the same wave-lengths as those for the emission within the lattice; at shorter wave-lengths there is no violet limit as for the photoelectric conduction, but emission increases with increasing wave-length. One can see here the reason why the absorption bands (photoionization bands) of internally

\* M. J. O. Strutt, *Ann. Phys.*, Lpz., **84**, 485 (1927); **85**, 129 (1928); **86**, 319 (1928). R. Peierls, *Ergebn. exakt. Naturw.* **40**, 264 (1933); R. de L. Kronig and W. G. Penney, *Proc. roy. Soc. A*, **130**, 499 (1931); R. de L. Kronig, *Z. Phys.* **70**, 317 (1931); L. Brillouin, *Die Quantenstatistik*, pp. 271 ff., Berlin (1931).

† R. Fleischmann, *Z. Phys.* **84**, 717 (1933).

adsorbed atoms have such a symmetrical form as is shown in Fig. 97 in § 76.\*

Fröhlich† attempted to connect the absorption bands of the coloured alkali halides directly with the permitted and forbidden energy zones in the lattice. He considers the absorption bands to be caused by free electrons in the lattice, and the absorption to be a consequence of the transition of these electrons from the energy zone where they occur to the next higher energy zone. The position of these energy zones is determined by the periodic potential field in the lattice as it is given by the sequence of positive and negative ions (Fig. 120).‡

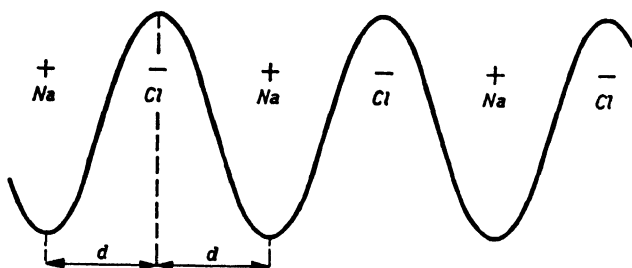


Fig. 120. Potential waves in rock-salt (100 direction).

The difference in energy between the first and the second permitted energy zone is approximately

$$\Delta Q = \frac{h^2}{16md^2},$$

where  $h$  is Planck's constant (§ 2),  $m$  the mass of an electron and  $d$  the shortest distance between two ions in the lattice (§ 12). The position of the absorption band is thus given by the relation

$$h\nu = \Delta Q = \frac{h^2}{16md^2},$$

$$\nu d^2 = \frac{h}{16m} = 0.45 \text{ cm.}^2/\text{sec.}$$

\* R. de L. Kronig and A. Smekal, cf. A. Smekal, *Phys. Z.* **33**, 206 (1932).

† H. Fröhlich, *Z. Phys.* **80**, 819 (1933).

‡ In Fig. 120 and corresponding figures the potential (work for positive unit charge) is plotted so that the highest values (for the positive ions) come below, since we are considering here directly the energy values for the electron (negative unit charge).

This relation then gives, according to Fröhlich, the position of the maxima of the absorption bands of the coloured alkali halides; it refers to a transition from about the middle of the one energy zone to about the middle of the next higher energy zone (Fig. 121).

Mollwo\* had already discovered empirically the following relation for the position of these various absorption bands:

$$\nu d^3 = 0.50 \text{ cm.}^2/\text{sec.},$$

so that there is here apparently a good agreement between theory and experiment.

In the previous sections of this chapter and the foregoing one, however, we have seen repeatedly that the colour centres may not be considered as free electrons in the lattice, so that the absorption band also may not be conceived as due to the transition suggested by Fröhlich. The colour centres must be considered as internally adsorbed atoms and the absorption band as due to a transition of the valence electron of this atom to an energy level in the lattice. Considering both the above-mentioned relations giving the position of the absorption

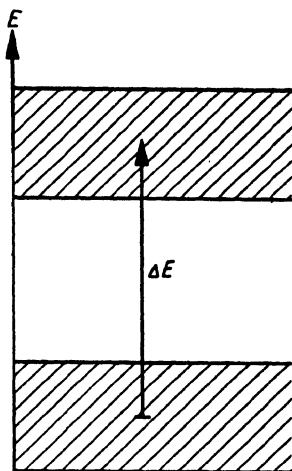


Fig. 121. The difference of energy  $\Delta E$  between about the middle of one permitted energy zone and the middle of another zone gives, according to Fröhlich, the frequency of the maximum of the absorption band ( $\Delta E = h\nu$ ).

band, one must assume that the energy level of this valence electron lies at about the same height as—slightly lower than—the centre of the first energy zone according to Fröhlich (Fig. 122).† In the highest energy zone shown in Fig. 122, which is normally completely free of electrons, the electrons are mobile in the lattice; they are displaced in an electric field (electronic conduction in the lattice after the liberation of electrons).

Now it has continually been assumed in the above that the electrons move in the lattice in the direction of the ribs of the

\* E. Mollwo, *Nachr. Ges. Wiss. Göttingen*, p. 97 (1931).

† J. H. de Boer and W. de Groot, *Z. Phys.* **83**, 517 (1933).



cubes (100 direction). From the excellent experiments by von Hippel\* of the electric breakdown in alkali halide lattices it appears that the electrons prefer to move in another direction, the 110 direction, through the lattice. This electric breakdown is also brought about by electronic conduction and occurs when the electrons, moving in the lattice under the influence of the electric field, have taken up so much energy from the field that they are no longer able to lose that energy by non-elastic collisions with the ions which lead to heat vibrations. The taking up of energy from the field increases rapidly for these electrons until they can ionize ions of the lattice by collisions; an avalanche of electrons then occurs,

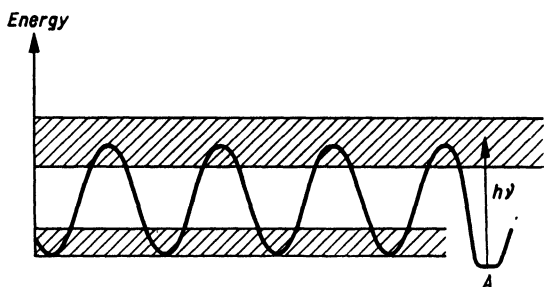


Fig. 122. The energy level  $A$  of an electron belonging to an atom, adsorbed on an internal surface, lies a little beneath the lowest energy zone in the lattice.

which leads to the electric breakdown. After the breakdown its path is marked and gives the preferred direction in which the electrons move most easily in the lattice. This now appears to be the 110 direction, and as second choice follows the 111 direction. In the 110 direction the differences of potential in the periodic potential field are smaller, since similar ions here follow one another, without the alternation of dissimilar ones (Fig. 123). The distance between two minima is hereby not  $2d$  as in the 100 direction (Fig. 120), but  $d\sqrt{2}$ .

If in order to determine the distance in the lattice from the first to the second permitted energy zone we take the periodic

\* A. v. Hippel, *Z. Phys.* **67**, 707; **68**, 309 (1931); **75**, 145 (1932); *Z. Elektrochem.* **39**, 506 (1933).

potential field in the 110 direction, then, due to the different separation of the minima,

$$\Delta Q = \frac{h^2}{8md^2},$$

that is to say, the distance between the two energy zones is twice as great. We may then no longer assume that the energy level of the electron of the internally adsorbed alkali metal atom lies at about the height of the first band, but we must imagine, in order to explain the position of the absorption bands, that this energy level lies half-way between the first and the second band\* (Fig. 124). The electron is brought from

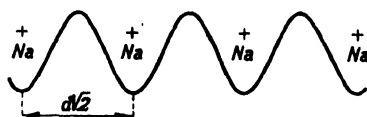


Fig. 123. Potential waves in rock-salt (110 direction).

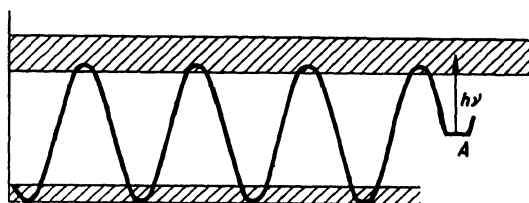


Fig. 124. The energy level *A* of an electron belonging to an atom, adsorbed on an internal surface, lies half-way between two permitted energy zones in the lattice.

this level by absorption of light into the highest energy zone which is normally empty.

It may seem remarkable that the energy levels of the internally adsorbed atoms, considering the very definite position of the absorption bands, all lie at about the same height. It is not impossible that this may be ascribed to the mutual similarity in structure of the great majority of the internal surfaces, for which we imagine an analogous structure to that given in Fig. 15 in § 14. A variation from this level is however possible, for example at the excitation centres (§ 77).

\* This seems to agree accidentally with the theory of A. H. Wilson, *Proc. roy. Soc. A*, **133**, 458; **134**, 277 (1931).

In contrast to an earlier assumption that we had to do with electrons in the lattice in this case,\* it is probable that here again we are concerned with internally adsorbed atoms, whereby, however, the energy level of the valence electrons lies higher (§ 77), see Fig. 125.

If Fig. 125 represents the correct positions of the zones of full and empty levels in the salt, one would expect an absorption of light at a frequency corresponding to an energy value of  $2 \times 2.65$  electron volts in the case of sodium chloride. This would mean an absorption of light at a wave-length of about  $230 \text{ m}\mu$ . There is no absorption band at that wave-length so that Fig. 125 cannot be correct.

The absorption band of the lattice of sodium chloride lies at a wave-length less than  $160 \text{ m}\mu$  (Table VIII, § 73), corresponding to an energy value of more than 7.7 electron volts. There is, however, no reason to associate this absorption band with the transition of an electron from a level in the zone of full levels to a level in the zone of empty levels, since no photoelectric conduction is connected with this absorption band.

According to our present knowledge there is not a single experimental indication for such a transition. Electrons are transmitted into the zone of empty levels only from the levels of the colour centres (levels *A* in Fig. 125), of the excitation centres (levels *B* in Fig. 125) and of the *U* centres (in Fig. 125 these levels should be at a distance of 6.42 electron volts from the zone of empty levels).

In the last figures only the energy of the electron in the lattice is taken into account. In the transition of an electron of an internally adsorbed atom to a band of permitted energies in the lattice, however, the adsorption energy of the internally adsorbed atom and of the ion formed by its ionization may

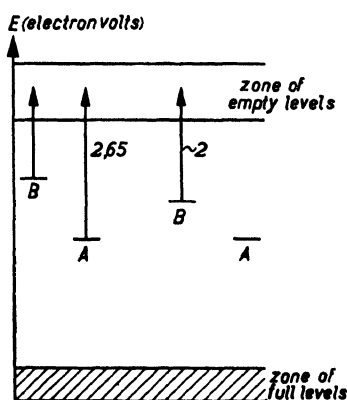


Fig. 125. Relative positions of energy levels of colour centres (*A*) and excitation centres (*B*) in rock-salt.

\* J. H. de Boer and W. de Groot, *Z. Phys.* **83**, 517 (1933).

not be neglected. We may now complete Fig. 107 of § 79 by the addition of the energy zones treated in this section. Fig. 107 is drawn for the case in which the atom, ionized thermally or by the absorption of light, is adsorbed on an external surface and the electron is emitted toward the outside; the levels  $a$  and  $d$  thus represent the free atom and the free ion respectively and the distance  $I$  is the ordinary ionization energy. Ionization may also take place when any arbitrary amount of energy greater than  $I$  is taken up since the electron freed can take up

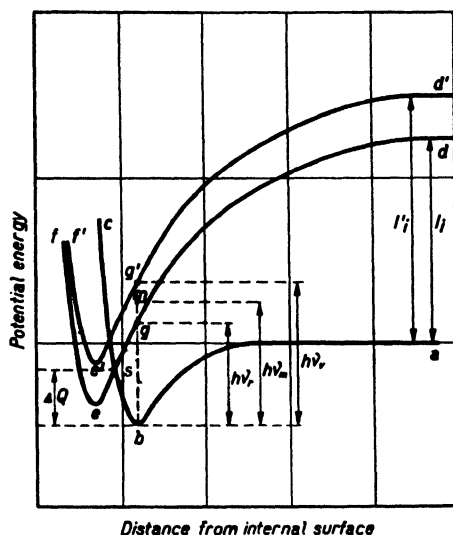


Fig. 126. Potential curves for the ionization of an internally adsorbed atom.

any arbitrary amount of kinetic energy. Thus above the curve  $def$  there is also a continuous region, to each point of which a transition is possible from the curve  $abc$ ; the photoelectric threshold is then given by  $bg$  (cf., however, the modification in this picture due to zero point vibration, § 53), photoemission at shorter wave-lengths causing a transition from  $b$  to a point lying above  $g$ .

Fig. 126 holds for the adsorption on an internal surface. Curve  $abc$  is again the potential curve for the internally adsorbed atom,  $a$  represents the free atom. If one imagines the free atom ionized and the electron brought into the lattice,

then an amount of energy must be supplied between the values  $I_i$  and  $I_i'$ , which are greater or smaller than the normal ionization energy  $I$ , according as energy must be added or is gained when an electron is brought from the vacuum into the permitted band in the lattice. Instead of curve  $def$  with a continuous region above it as in Fig. 107 we now obtain a zone between  $def$  and  $d'e'f'$  to which a transition is possible. The red threshold of the internal photoeffect is given by  $bg$ , the violet limit by  $bg'$ , and the maximum by  $bm$ . In thermal ionization (semi-conduction) the amount  $bs$  must be exceeded by the thermal energy. The amount of energy corresponding to the red threshold ( $h\nu_r$ ) is thus neither for the emission in a vacuum nor for the emission in the lattice equal to the amount of energy necessary for thermal ionization:\*

$$h\nu_r \neq \Delta Q.$$

We shall return to this point in §§ 90 and 99.†

In the case of excitation centres the curves corresponding to  $def$  and  $d'e'f'$  have deeper minima, in the case of  $U$  centres the minima are much less deep or there may be no minima, since the adsorption energy for the ion at the internal surface is greater in the case of excitation centres and much smaller in the case of  $U$  centres (cf. §§ 77 and 83).

\* J. H. de Boer and M. C. Teves, *Z. Phys.* **83**, 521 (1933); J. H. de Boer and W. Ch. van Geel, *Physica*, **2**, 286 (1935).

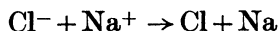
† Recently A. Smakula, *Nachr. Ges. Wiss. Göttingen*, Neue Folge, **1**, 55 (1934), determined  $\Delta Q$  in alkali halide crystals to be 30 to 50 per cent. of  $h\nu_r$ . Thus for sodium atoms in sodium chloride  $\Delta Q = 0.94$  electron volt and  $h\nu_r = 2.65$  electron volts.

## CHAPTER XII

### ELECTRONIC CONDUCTION IN LATTICES OTHER THAN THOSE OF THE ALKALI HALIDES

#### § 86. The photochemical decomposition of silver halides and similar compounds.

When the alkali halides absorb light of a wave-length which lies within their own ultraviolet absorption band an electron jump takes place from the halogen ion to the metal ion, and both become neutral atoms (§ 73). In the middle of the lattice following this process there is an immediate return of the electron, and there is consequently no permanent change. At internal surfaces and defects of the lattice, however (§ 74), a permanent coloration has taken place as a result of the absorption of light. The reaction



has at these spots a permanent result, a photochemical reaction has taken place.

The analogous process with the silver halides, viz. the transition of an electron from the halogen ion to the silver ion by absorption of light, has long been regarded as the elementary reaction in photography.\* Such transitions also take place with very many halides, and also with other compounds of other metals, and are often accompanied by permanent changes. In the case of the silver halides this reaction has been studied somewhat more in detail, so that we may use this material to give a short summary of the experiments and their results, as far as they may be useful for the purposes of this book.

The absorption spectra of compounds such as the silver halides, the copper halides, the thallous halides and also the lead halides are much less sharp and pronounced than those

\* S. E. Sheppard and A. P. H. Trivelli, *Photogr. J.* **61**, 403 (1921); K. Fajans, *Chemikerztg.* **45**, 666 (1921); *Z. Elektrochem.* **28**, 299 (1922).

of the alkali halides\* (cf. Figs. 127 and 128 with Fig. 96 in § 73). The bands do not become sharp even at low temperatures,

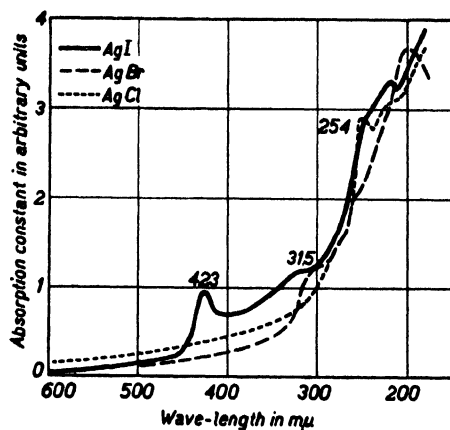


Fig. 127. Absorption of light by the silver halides. H. Fesefeldt and Z. Gyulai, *Nachr. Ges. Wiss. Göttingen*, p. 229 (1929).

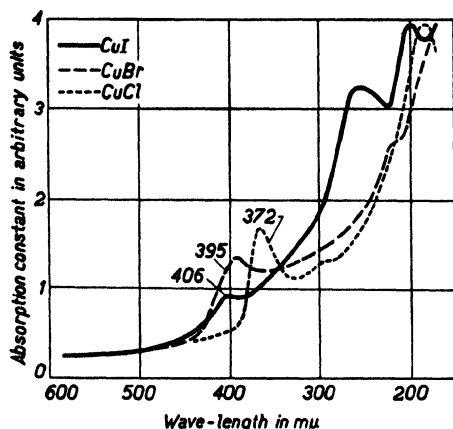
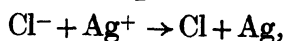


Fig. 128. Absorption of light by the cuprous halides. H. Fesefeldt and Z. Gyulai, *Nachr. Ges. Wiss. Göttingen*, p. 229 (1929).

and the appearance at  $-186^{\circ}\text{C}$ . is practically the same as that at room temperature. Even without the cooperation of

\* Cf. R. E. Slade and F. C. Toy, *Proc. roy. Soc. A*, **97**, 181 (1920); C. Schell, *Ann. Phys.*, Lpz., **35**, 711 (1911); R. Hilsch and R. W. Pohl, *Z. Phys.* **48**, 384 (1928); H. Fesefeldt and Z. Gyulai, *Nachr. Ges. Wiss. Göttingen*, p. 226 (1929); H. Fesefeldt, *Z. Phys.* **67**, 37 (1931).

the agitation due to temperature there seems to exist a strong reciprocal action between adjacent components of the lattice. Upon irradiation with light corresponding to the long-wave extension of these absorption bands the above-mentioned photochemical reaction takes place:



whereupon here also, just as with the alkali halides (§§ 74 and 76), a new absorption band, that of the latent image, is

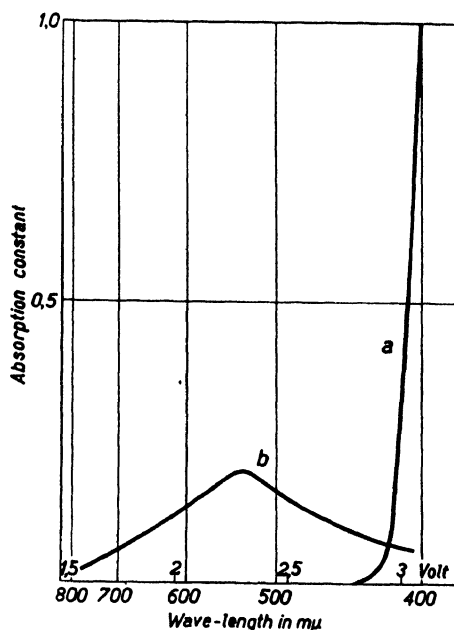


Fig. 129. Absorption spectra of AgCl (a) and of the latent image in AgCl (b).\*

formed.\* The number of silver atoms which can be obtained in the crystal in this way is very dependent on the previous history of the crystal, in other words, we are concerned here, as in the case of the alkali halides, with a property which is very sensitive to structure. The capacity to become coloured increases here also with increasing mechanical deformation and is decreased by homogenizing by means of a suitable temperature treatment. Thus the silver atoms formed are

\* R. Hilsch and R. W. Pohl, *Z. Phys.* 64, 606 (1930).



situated here also upon internal surfaces or imperfections of the lattice.

So far it is as if there were a complete analogy with the alkali halides. There are, however, many points of difference to be indicated, several of which are very important. In the first place the absorption band of the latent image formed is much less sharp and pronounced than with the alkali halides, while it lies closer to the absorption band of the lattice itself, so that the two bands partially overlap (see Fig. 129). Upon

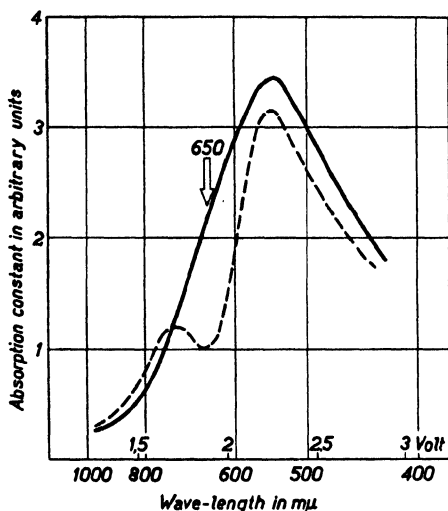


Fig. 130. By irradiation with light of a certain frequency the absorption spectrum of the latent image in AgCl is bleached out for this frequency. R. Hilsch and R. W. Pohl, *Z. Phys.* **64**, 606 (1930).

irradiation within the new band no excitation (§ 77) takes place, although a bleaching action is found (Herschel effect, § 78). In this bleaching, however, there is a special behaviour: if a beam of light containing only a narrow range of frequencies is used for irradiation (cf. Fig. 130), then the absorption band is only bleached for those frequencies which correspond to those of the light used (colour adaptation, compare also § 64). The properties of the absorption bands formed indicate that here the product of the photochemical reaction does not consist, as was the case with the alkali halides, of internally adsorbed atoms, but of colloidal particles. The total absorption

band is composed of various absorption bands superposed upon one another and due to colloidal particles of different dimensions. In keeping with the colloidal character is the insensitivity of the latent image to temperature changes (§ 84). When only a small amount of silver is formed photochemically, colloidal particles mainly of small dimensions are formed (maximum of the absorption band at  $510\text{m}\mu$  with  $\text{AgCl}$ ), when more silver is formed the average size of the particles increases and the maximum of the absorption band shifts toward longer wave-lengths (finally to  $560\text{m}\mu$ ).<sup>\*</sup> The more places of disturbance the crystal exhibits, the smaller are the dimensions of the colloidal particles; at high temperatures the dimensions are greater than at low temperatures.

Thus directly following upon the elementary photographic process, in which halogen and silver atoms are formed, comes a coagulation in the case of the silver halides to give a colloidal distribution of silver, whereas with the alkali halides it was necessary to heat in order to obtain coagulation (§ 84). This coagulation in the case of the silver halides also may be ascribed to a movement of electrons through the lattice. One may actually measure—and this is a very great difference from the alkali halides—a photoelectric current immediately during the photochemical coloration.<sup>†</sup> One must continue to assume that there is no movement of electricity due to the elementary photographic process itself, that is, during the transition of the electron from the halogen ion to the silver ion, and that the photoelectric current measured is a phenomenon which accompanies the coagulation. One might now imagine that the above-mentioned overlapping of the absorption band proper and the absorption band of the latent image is responsible for this coagulation, in other words, that the irradiation within the long-wave portion of the absorption band is at the same time an irradiation within the ionization band of the internally adsorbed atom formed, the result of which

<sup>\*</sup> F. Löhle, *Nachr. Ges. Wiss. Göttingen*, p. 273 (1933).

<sup>†</sup> B. Gudden and R. W. Pohl, *Z. Phys.* **16**, 42 (1923); F. C. Toy and G. B. Harrison, *Proc. roy. Soc. A*, **127**, 613 (1930).

would be photoelectric coagulation\* (§ 84). This, however, did not appear to be the explanation; the photoelectric current flowed immediately at its full value in a previously completely unilluminated crystal, so that a purely thermal coagulation must be imagined.† The silver atom formed by the photochemical process loses its electron so easily that a movement of electricity is immediately noticeable. The distance covered by an electron in a silver chloride crystal is quite great. In § 76 we saw that in the case of the alkali halides the electrons covered a distance  $3 \times 10^{-4}$  cm. with a field of 2000 volts/cm., that is to say a distance of about  $1.5 \times 10^{-7}$  cm. with a field of 1 volt/cm. In the case of silver chloride, however, an electron covers a distance of about  $2.5 \times 10^{-5}$  cm.‡ with a field of 1 volt/cm., that is to say more than a millimetre with a field of 5000 volts/cm. If extra places of disturbance are introduced, these average shifts of the electron become smaller here too, thus the addition of 0.05 mol. per cent. CuCl to silver chloride gives a decrease to  $1.1 \times 10^{-5}$  cm. in a field of 1 volt/cm. It is remarkable that when the silver chloride crystal has previously been strongly coloured photochemically, the average distance covered by the electrons is very much increased (to  $20 \times 10^{-5}$  cm. with a field of 1 volt/cm. for instance). This behaviour must be understood in the following way: the average distance over which the electron is shifted is controlled by the probability of its being captured and held on an internal surface or place of disturbance. When the number of places of disturbance is increased the chances that the electron will be captured increase and the average distance of shift decreases. If the places of disturbance are already occupied after photochemical coloration, then the average distance of shift for the electron increases.

In the hope that the silver would be deposited in atomic form at low temperatures§ Löhle|| irradiated silver chloride at

\* R. Hilsch and R. W. Pohl, *Z. Phys.* **68**, 721 (1931).

† R. Hilsch and R. W. Pohl, *Z. Phys.* **77**, 424 (1932).

‡ K. Hecht, *Z. Phys.* **77**, 235 (1932).

§ Cf. R. Hilsch and R. W. Pohl, *Z. Phys.* **77**, 423 (1932).

|| F. Löhle, *Nachr. Ges. Wiss. Göttingen*, p. 271 (1933).

$-186^{\circ}\text{C}$ . However, even at this temperature a colloidal dispersion of silver was obtained. One is thus compelled to assume that if any internally adsorbed silver atoms are present they lose their valence electrons extraordinarily easily. This is possible if the amount of energy  $\Delta Q$  in Fig. 107 in § 79 is very small, which may be the case when curve *def* cuts curve *abc* almost at the minimum *b*, for instance within the region of the zero point vibration (§ 53), see Fig. 131. An adsorbed atom is then transformed directly into an adsorbed ion and

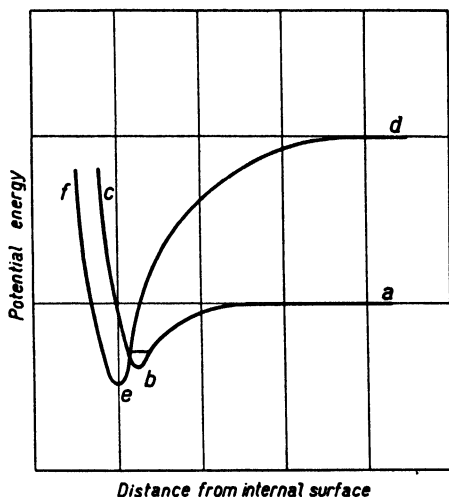


Fig. 131. Potential curves for the adsorption of a silver atom or similar atoms on an internal surface in a silver halide crystal. The ionic curve cuts the atomic curve in the region of the zero point vibration, so that ionization takes place; the internally adsorbed atom is directly converted into an internally adsorbed ion and an electron moving in the lattice.

loses its electron. Only when silver atoms are present next to each other do they continue to exist as atoms; the mutual van der Waals attraction of these atoms which finally manifests itself as a condensation energy of the colloidal particles must play a part in this stabilization. In order that the formation of the colloidal particles shall take place at  $-186^{\circ}\text{C}$ . it appears that a minimum quantity must first be present. At least according to Löhle a completely unilluminated crystal at  $-186^{\circ}\text{C}$ . is not coloured by irradiation, while it is coloured after it has been previously irradiated at room temperature with a few quanta of light.

It must finally be noted that in photographic literature it has already long been assumed that the latent image consists of colloiddally dispersed silver. Moreover, in 1926 Eggert and Noddack\* considered the coagulation of the silver atoms to colloidal particles as a result of a movement of electrons. The previous introduction of very small—not yet developable—particles of silver or silver sulphide (ripening) increases the sensitivity.

§ 87. Photoelectric conduction in substances other than coloured alkali halides.

The silver halides thus give a photoelectric current *directly* upon illumination, and it is not first necessary, as it is with the alkali halides, to provide for the presence of internally adsorbed atoms. Very many substances behave photoelectrically similarly to the silver halides, and thus give a photoelectric current directly upon illumination. Gudden and Pohl† call such crystals which give a photoelectric current upon irradiation within their own absorption band “*idiochromatic crystals*” in contrast to the “*allochromatic crystals*”, which are inactive photoelectrically when pure, but which are active when certain foreign atoms or particles are dispersed throughout the crystal.

All the idiochromatic crystals are distinguished by a high index of refraction, and the rule is that this index must be greater than 2 if the substance is to be photoelectrically active. Substances of otherwise very different properties belong to this group. Besides the already mentioned silver halides may be mentioned the halides of copper (cuprous), mercury (mercuric), thallium (thallous) and lead, very many sulphides such as  $\text{Ag}_2\text{S}$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{HgS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{MoS}_2$ ,  $\text{PbS}$ , and very many complex sulphides,‡ as for example pyrargyrite ( $\text{Ag}_3\text{SbS}_3$ ), oxides like  $\text{Cu}_2\text{O}$ § or  $\text{Sb}_2\text{O}_3$ ,|| and in addition  $\text{PbCO}_3$ , sulphur, selenium, yellow phosphorus, iodine, diamond, naphthalene.¶ Some of

\* J. Eggert and W. Noddack, *Z. Elektrochem.* **32**, 496 (1926).

† Cf. B. Gudden, *Lichtelektrische Erscheinungen*, p. 148 (1928), Berlin.

‡ T. W. Case, *Phys. Rev.* **9**, 305 (1917).

§ A. H. Pfund, *Phys. Rev.* **7**, 289 (1916).

|| W. Heintze, *Z. Phys.* **15**, 339 (1923).

¶ Cf. further: B. Gudden, *loc. cit.*, and A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, Chap. VIII, pp. 284–352 (1932).

these substances are insulators in the dark, while some of them conduct an electric current also without illumination as so-called semi-conductors. The photoelectric conduction of insulators and that of semi-conductors has often been treated separately in the literature, but since there is only a quantitative difference between the two groups (§ 90) we shall not make a distinction between them here.

Especially with the idiochromatic crystals must one distinguish carefully between the primary photoelectric current, which can be separated into the negative primary current and the positive primary current (§ 77), and secondary currents (§ 88). The primary current gives the actual photoelectric phenomenon, here again, as in Chap. x, consisting of the liberation of the electrons by the light and the motion of these electrons through the lattice (negative primary current), and the supplementation of these electrons in order to neutralize the space charge formed by the excitation (positive primary current). The primary current\* in the ideal case has the properties, already known to us from Chap. x, of being exactly proportional to the light energy absorbed, of flowing without time lag at the beginning of the illumination, also of stopping without time lag,† as well as of increasing linearly with increasing field strength until a saturation value is reached. At low temperatures, and sometimes even at room temperature (diamond), the positive primary current is completely lacking, and thus no supplementation of electrons is provided. The negative primary current is (as long as there is no change in the absorption of light) independent of the temperature. In the literature mention is often made of a sharp decrease of the photoelectric conduction with falling temperature, and in practically all cases this is due to the lack of supplementation of electrons; the negative primary current is still present and unchanged, but it quickly builds up space charges which are not neutralized, so that the current may fall to zero.

The spectral distributions of the photoelectric sensitivity

\* B. Gudden and R. W. Pohl, *Z. Phys.* **6**, 248; **7**, 65 (1921); **16**, 170; **17**, 331 (1923); *Phys. Z.* **23**, 417 (1922).

† W. Flechsig, *Z. Phys.* **33**, 372 (1925).

for all of these idiochromatic crystals have one common characteristic, viz. that the maximum of the photoelectric sensitivity lies at those wave-lengths at which the absorption of light shows a strong rise. There is here, in contrast to what we saw with the coloured alkali halides (§ 76), no coincidence of the light absorption curve and that of the spectral distribution of photoelectric sensitivity. In Fig. 132

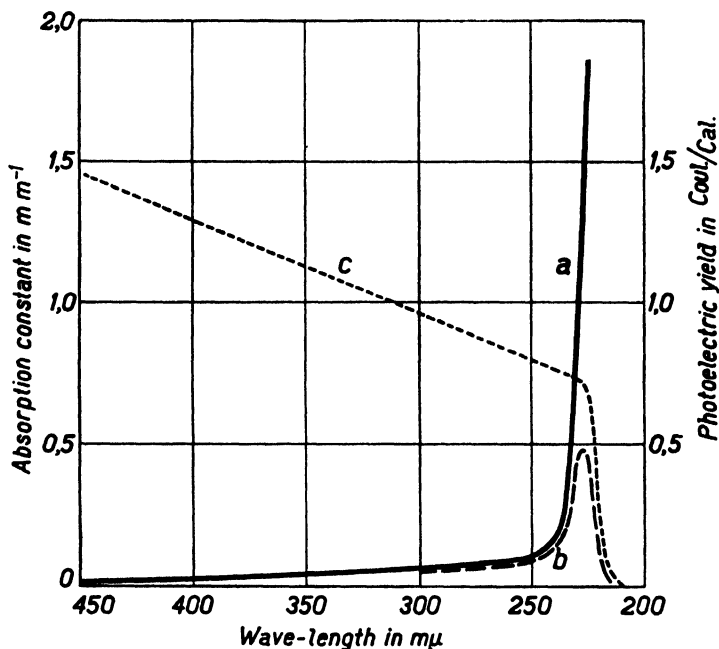


Fig. 132. Light absorption and photoelectric conductivity of an idiochromatic crystal (diamond): *a*, light absorption; *b*, photoelectric yield referred to incident light; *c*, photoelectric yield referred to absorbed light. B. Gudden and R. W. Pohl, *Z. Phys.* 17, 331 (1923).

an example is given of the mutual positions of these bands for the case of a sort of diamond which is very transparent to ultraviolet light. Referred to incident light energy the photoelectric conductivity is at a maximum at that point where the absorption of light begins to be so strong that the absorption coefficient about reaches the value  $1 \text{ mm.}^{-1}$ . Referred to absorbed light energy, however, the result of the measurements is extremely simple. The quantity of electricity separated per calorie of absorbed light, or, in other words, the electrical yield,

is proportional to the wave-length. This is explained by the fact that one electron is freed per quantum ( $h\nu$ ) absorbed, the electrical yield being then, when  $n$  quanta are adsorbed,  $\frac{n\epsilon}{nh\nu}$ ,

since also  $n$  electrons are freed. Such an amount  $\frac{\epsilon}{h\nu}$  is immediately directly proportional to the wave-length, since  $\epsilon$  and  $h$  are constants. The slope of the line representing the electrical yield according to the measurements of Gudden and Pohl\* on diamond does actually give a fairly good value for Planck's constant  $h$  (§ 2). Also with zincblende (ZnS) and cinnabar (HgS)† similar results are obtained.

In the actual region of strong light absorption there is with all these substances *no* observable photoelectric effect, while light absorbed within the long-wave extension leads quantitatively to the splitting off of internal electrons. In § 74 we saw that the actual absorption within the strong absorption bands of the alkali halides does not lead to a permanent photochemical coloration, but that the light absorbed within the long-wave extension is responsible for the photochemical coloration. Just as in § 74 we may here also conclude that light which is absorbed by actual components of the lattice does *not* lead to a photoelectric effect, but that light which is absorbed by components of the lattice situated at places of disturbance or on internal surfaces does give photoelectric conduction. In this case again the long-wave extension of the absorption band does not belong to the absorption curve of the components of the lattice, but it represents the absorption by atoms, molecules or ions situated on internal surfaces.

If the liberated electrons cover a certain distance in the lattice (negative primary current) and no supplementation or an insufficient one is provided (lack or partial lack of positive primary current, cf. § 76), then we obtain here also the phenomenon of excitation (cf. § 77). The excitation manifests itself here optically in a reinforcement and an expansion of the long-wave extension of the absorption band toward

\* B. Gudden and R. W. Pohl, *Z. Phys.* **17**, 331 (1923).

† B. Gudden and R. W. Pohl, *Z. Phys.* **18**, 199 (1923).



long wave-lengths. Thus in Fig. 133 the spectral distribution of the photoelectric conduction of selenium in unexcited and excited states is given. At the excitation centres the electrons are again less strongly bound than in the active centres in the unexcited state. Just as with the coloured alkali halides the excited state is neutralized by irradiation with long-wave light, by warming, or by the passage of time. The spectral distribution of the photoelectric activity for a crystal in the excited state differs from that of the crystal in the unexcited

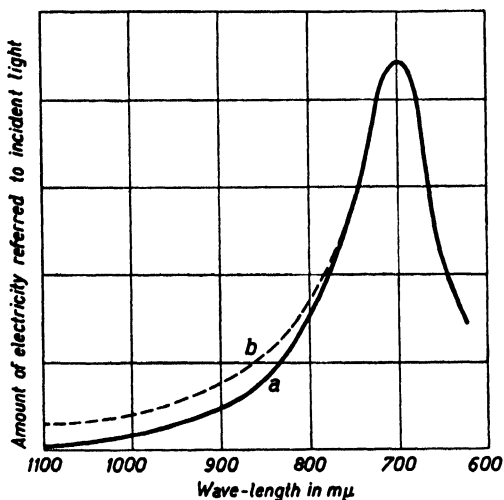


Fig. 133. Spectral distribution of the primary photoelectric current in a red insulating selenium crystal: *a*, in the unexcited state; *b*, in the excited state B. Gudden and R. W. Pohl, *Z. Phys.* **35**, 243 (1925).

state exactly according to the difference in absorption of light. The liberation of the electrons from the excitation centres gives another photoelectric current (namely, the positive primary current) for which the quantum equivalence again holds true.

In view of this phenomenon of excitation and the accompanying optical change it is clear that red or infrared light which causes no photoelectric current in the case of diamond does cause such a current after the diamond has been irradiated with blue light, and also that the red or infrared light which is inactive in the case of a previously unirradiated diamond or zincblende crystal when used simultaneously with blue light

nearly doubles the photoelectric current due to the blue light.\* The positive primary current gives the same transfer of electricity as the negative primary current.

If the crystals have many impurities or internal imperfections or surfaces (for example, compressed fine powders), then the photoelectric current observed is smaller and sometimes no current at all can be observed. One must, however, assume in this case that the photoelectric phenomenon as such is not lessened—upon irradiation just as many, perhaps more, electrons are liberated—the average displacement in an electric field has, however, become smaller for the electrons, since they are recaptured much sooner by the increased number of places of disturbance in the lattice. Coloured diamonds, brown zincblende or microcrystalline precipitates of zinc sulphide or mercury sulphide exhibit practically no photoelectric conduction, the power of phosphorescing in the last cases indicates that there is still a photoelectric activity.†

### § 88. Secondary currents.

Besides the phenomena of the primary current (the motion of the electrons directly freed by the light, and the supplementation of these electrons), we are concerned in very many cases with other quite different conduction phenomena which are caused or reinforced by irradiation. By the passage of the electrons of the primary current and by the consequent change in the lattice, a decrease of the resistance of the lattice is often brought about, so that a large current, which may be of electrolytic or of electronic nature, may flow. In this case the number of carriers of electric charge arriving at the electrodes is often greater by several orders of magnitude than the number of quanta of light absorbed.

There are several important differences to be noted between the secondary currents caused by this decrease in resistance and the primary currents of the photoelectric phenomenon itself. The primary current begins, without time lag, at a very definite starting value; the secondary current is developed

\* B. Gudden and R. W. Pohl, *Z. Phys.* **16**, 174 (1923); **20**, 14 (1924).

† B. Gudden and R. W. Pohl, *Z. Phys.* **16**, 170 (1923).

during the irradiation, and a regular rise of the photoelectric current with the time can be observed, often until a constant value is reached. After the conclusion of the irradiation the secondary current continues to flow with continually decreasing strength.

The secondary currents are in many cases the dominating ones and they determine completely for example the characteristics of the technical selenium and thallopide cells. The sulphides, which have been thoroughly examined, such as zinc sulphide,  $\text{ZnS}$ , and especially molybdenum sulphide,  $\text{MoS}_2$ ,\* are very good examples of substances in which the secondary currents dominate.

The secondary currents are distinguished from the primary currents by many other factors besides the above-mentioned time lag. Thus the secondary currents are *not* proportional to the light intensity, and there is often even a hysteresis effect. Precisely because of the dominant secondary currents there is no proportionality with the amount of light in the case of many technical cells (selenium cells, for example) which are based upon the phenomenon of photoelectric conduction. In the case of selenium cells different investigators have proposed different relations in which the current  $i$  is proportional to the light intensity  $I$ , raised to a certain power  $y$ ,

$$i = aI^y,$$

where  $y$  varies among the different investigators between  $\frac{1}{4}$  and 1, and is usually  $\frac{1}{2}$ . Since in addition the relation between  $i$  and the light intensity  $I$  is not the same for all wave-lengths, one often obtains very different spectral distribution curves according as one measures at a low or at a high illumination.

Further, the secondary currents often depend upon the field. While with small fields there is proportionality between the strength of the primary current and the field strength, and with larger fields the primary current begins to increase more slowly than proportional with the field (and may finally become saturated), the secondary currents on the other hand

\* W. W. Coblentz and H. Kahler, *Bull. U.S. Bur. Stand.* 15, 121 (1919).

often increase more rapidly than proportional with the field; a breakdown may occur.

The secondary currents are further, in contrast to the negative primary current, very dependent upon the temperature, and this dependence upon temperature is far from simple.

When a definite number of light quanta is absorbed by a strongly absorptive crystal, it is not of importance for the strength of the primary current whether this light is absorbed over the whole distance between anode and cathode, or only close to one of the electrodes; for the secondary current, however, this is very important because this current is greater according as the current density of the primary photoelectric current is greater.

We saw in the previous section that many imperfections of the lattice act as a hindrance to the primary current, since the electrons are recaptured after having covered a very short distance. The secondary currents are intensified by the presence of many places of disturbance in the lattice, so that in the case of compressed powders for example they are very strong.

One might conclude from the above that the secondary currents are of electrolytic nature, and this is often assumed.\* Perhaps in many cases the secondary current is indeed of electrolytic nature. Lehfeldt† could, however, show that with zinc sulphide at ordinary and even higher temperatures and with silver chloride at low temperatures the secondary currents are also electron currents. He could also show that the secondary current is entirely dominated by the presence of excitation centres which give the crystal an electronic conduction. With zinc sulphide he could study the behaviour of the excitation centres as regards their phosphorescence, and he found a complete parallelism with the secondary current.

### § 89. Photoelectric electron conduction under the influence of impurities in the crystal.

Just as with the alkali halides the presence of internally adsorbed atoms or of colloidal particles of alkali metals leads

\* B. Gudden and R. W. Pohl, *Z. Phys.* 7, 65 (1921).

† W. Lehfeldt, *Nachr. Ges. Wiss. Göttingen*, p. 263 (1933).

to a photoelectric and a thermal conductivity, so it does with other crystals also. A whole series of minerals and inorganic salts can be coloured, for example by the action of short-wave ultraviolet rays or of cathode rays or X-rays. A new absorption band is thereby created, which may be considered a photo-ionization band of internally adsorbed atoms or of colloidal particles. Colloidal particles are certainly present in yellow citrine ( $\text{SiO}_2$ ), in coloured fluorite ( $\text{CaF}_2$ ) and in the coloured silver halides (§ 86). Irradiation with light within the absorption band of these atomic or colloidal impurities results in a liberation of electrons in the lattice and photoelectric conduction.

If we have this phenomenon with crystals which already exhibit photoelectric conduction upon illumination within the long-wave extension of their own absorption band (idiochromatic crystals, § 87), as is the case with the silver halides, then we obtain, due to the colloidal impurities, a second band of photoelectric activity, lying toward longer wave-lengths; the crystals are then at the same time idiochromatic and allochromatic. One may now ask whether such impurities play a part in many cases of idiochromatic crystals where in the spectral distribution curves of the photoelectric conductivity a second maximum occurs lying toward longer wave-lengths in addition to the spectral maximum that coincides with the region of the sharp increase of the absorption. Thus  $\text{MoS}_2$  crystals give, besides a maximum of the photoelectric conductivity at a wave-length of  $1\mu$ , a second maximum at about  $1.8\mu$ .\* The maximum at  $1\mu$  is to be ascribed to the absorption of light of the lattice components situated upon internal surfaces or places of disturbance; the absorption band of  $\text{MoS}_2$  begins to show a sharp rise just at  $1\mu$  coming from longer wave-lengths, which indicates that at that point begins the absorption of the actual lattice components. One might reasonably suppose that the maximum at  $1.8\mu$  must be ascribed to some other atomic or, more probably yet, colloidal impurity, for example, molybdenum or a lower sulphide. In the case of cuprite ( $\text{Cu}_2\text{O}$ ), next to the maximum of the photo-

\* W. W. Coblenz and H. Kahler, *Bull. U.S. Bur. Stand.* 15, 121 (1919).

electric conductivity at  $0.63\mu$ , coinciding again with the sharp rise of the absorption band, another maximum at  $0.80\mu$  is often found\* (see also § 91). This maximum at  $0.80\mu$  may perhaps be ascribed to an impurity in the form of atomic or colloidal copper. While the measurements with  $\text{MoS}_2$  are mainly concerned with secondary currents, in the case of cuprite they are concerned with primary currents.

### § 90. Semi-conductors.

We have just seen that  $\text{MoS}_2$  exhibits maxima of the spectral distribution of the photoelectric conduction at  $1.0\mu$  and at  $1.8\mu$ . The long-wave maximum extends to  $2.5\mu$ , which corresponds to an energy of about 0.5 electron volt. When such a small amount of energy is apparently necessary to free electrons which provide for conduction, it is no wonder that even at room temperature there are always enough electrons present, due to the thermal agitation, to give conduction. A substance like  $\text{MoS}_2$  at room temperature conducts a current fairly well, and this conduction is also of electronic nature.

Semi-conductors are substances which conduct an electric current at ordinary temperatures, and sometimes only at higher temperatures, but which have in general a much higher resistance than metals. The resistance often decreases as the temperature rises, since at higher temperatures more electrons are freed (see § 81), in contrast to what occurs in metallic conduction where the resistance increases at higher temperatures (cf. also the remarks in § 81). A conductivity which is due to free electrons in the lattice decreases at higher temperatures, since the electrons lose increasingly more energy by the collision with the positive ions due to increased thermal agitation of these ions (metallic conduction). If, however, the number of conduction electrons increases at higher temperatures because of the fact that bound electrons are freed by thermal agitation, then the conductivity increases at higher temperatures, since the increase of the number of electrons takes place according to an exponential function, and thus the decrease of the conductivity due to the increased energy transfer by collision

\* B. Schönwald, *Ann. Phys.*, Lpz., 15, 395 (1932).

with the positive ions is more than compensated for. The conductivity can be represented by a formula

$$\kappa = ae^{-\frac{Q}{RT}},$$

where  $\kappa$  represents the conductivity,  $a$  is a constant,  $Q$  the work of freeing an electron,  $R$  the gas constant and  $T$  the absolute temperature. Thus  $Q$  is in this formula the energy with which the electrons are bound to internally adsorbed atoms, to colloidal impurities or to imperfections of the lattice, or in other words it is the energy which is necessary to transfer the electron from the place where it is bound into a permitted energy zone (cf. § 85) of the lattice.

A similar formula (see also § 81) holds for the electrolytic conduction, in which formula  $Q$  is the work necessary to free the moving ion. On the basis of the dependence of the conductivity on temperature it is thus *impossible* to distinguish directly whether in a definite case we are concerned with electronic or electrolytic conduction.

Other distinguishing methods must be used, as for example magnetic measurements for the electronic conduction (Hall effect), or the indication of a transfer of matter for the electrolytic conduction.\*

Between electronic semi-conductors, which alone will be dealt with here, and insulators there is in principle no real difference. The conductivity is entirely dependent on the number of conduction electrons which can be freed at a definite temperature. If this number of electrons is very small, then practically no flow of current is measured and we speak of an insulator; if however we artificially introduce electrons into such a lattice, then conduction is observed. For practical purposes we may draw the line of separation between insulators and semi-conductors at a conductivity of  $10^{-10}$  ohm $^{-1}$  cm. $^{-1}$ † Since the conductivity, as we have seen above, changes exponentially with the temperature, at low tem-

\* Cf. C. Tubandt, *Handbuch der Experimentalphysik*, 12, 1, pp. 383 ff., Leipzig (1932).

† B. Gudden, *Phys. Z.* 32, 826 (1931).

peratures most semi-conductors are changed into insulators and at high temperatures many insulators are changed into semi-conductors.

For the energy  $Q$ , necessary to free an electron, values between 0.01 and 0.8 electron volt are found for various semi-conductors. These very low values cause one to suspect that there is no connection here between the conduction electrons and the absorption bands of the lattices themselves. Let us again take  $\text{MoS}_2$  as an example. It has an absorption band which begins to rise steeply at about  $1\mu$  (most of the other semi-conductors have bands lying toward still shorter wave-lengths, thus for example the absorption edge of  $\text{Sb}_2\text{S}_3$  lies at  $0.78\mu$ , of  $\text{Cu}_2\text{O}$ , which has recently been much investigated, at  $0.63\mu$ ). It is clear that since the energy corresponding to the beginning of this absorption is more than 1 electron volt, there must be in the lattices still other sources which supply conduction electrons. We have as a matter of fact already seen (§ 89) in the case of  $\text{MoS}_2$  that farther toward long wave-lengths in the infrared a second band of photoelectric conduction can be discerned, whose maximum lies at about  $1.8\mu$  and which extends to  $2.5\mu$  ( $\sim 0.5$  electron volt). It is to be expected that an amount of energy will be found for  $Q$  which will approximately correspond in order of magnitude to the energy belonging to the longest wave-lengths whereby photoelectric conduction is possible. An exact correspondence may not be expected immediately, since according to Fig. 126 in § 85 the energy necessary to obtain thermal ionization is not equal to, and is usually smaller than, the minimum energy necessary for photoionization ( $h\nu_r$ ).<sup>\*</sup> From the data about the conductivity and the Hall effect of  $\text{MoS}_2$ , given in the International Critical Tables for the energy of the thermal ionization, 0.15 electron volt can be calculated, a value which is actually much smaller than the value for  $Q$  found for the photoelectric conductivity.

It remains to be noted that in the case of special assumptions about the nature of the electronic conduction, the energy  $Q$  in the formula for the thermal conductivity represents only one-

<sup>\*</sup> J. H. de Boer and W. Ch. van Geel, *Physica*, 2, 286 (1935).



half of the actual ionization energy.\* There are, however, many objections to these assumptions.†

In such a substance as  $\text{MoS}_2$  there are always free electrons present even at room temperature. It is reasonable to suppose that these free electrons are responsible for the absorption of light which extends toward still longer wave-lengths than the limit of the photoconductivity  $2.5\mu$ .

We know practically nothing more about the nature of the atoms or places of disturbance which supply electrons; they are, however, probably really internally adsorbed atoms or colloidal particles which emit their electrons thermally, a mechanism which should be similar in principle to the one with which we became acquainted in the case of the coloured alkali halides at temperatures of several hundred degrees (§ 81).

$\text{MoS}_2$  is a semi-conductor whose conduction is of an electronic nature. The following sulphides are also electronic conductors:  $\text{CuS}$ ,  $\text{PbS}$ ,  $\text{CdS}$ ,  $\text{Sb}_2\text{S}_3$  and  $\text{SnS}$ . It was always thought that  $\alpha\text{-Ag}_2\text{S}$  (modification above  $174^\circ\text{C}$ .) was an electrolytically conducting substance.‡ More recent investigations, however, proved it to be an electronic semi-conductor.§

### § 91. Semi-conductivity under the influence of electronegative elements.

The conductivity of cuprous iodide ( $\text{CuI}$ ) is very much increased when it is mixed with an excess of free halogen, in this case iodine.|| We have here an example where it is not the internal adsorption of electropositive atoms able to emit their valence electrons which makes the conductivity increase, but it is the taking up of an electronegative element. With other cuprous halides,  $\text{CuCl}$  and  $\text{CuBr}$ , the conductivity is increased

\* F. Bloch, *Phys. Z.* **32**, 886 (1931); A. H. Wilson, *Proc. roy. Soc. A*, **133**, 458; **134**, 277 (1931); R. H. Fowler, *Proc. roy. Soc. A*, **140**, 505; **141**, 56 (1933).

† A. F. Joffé, *Actualités scientifiques et industrielles*, **87**, 22 (1933); B. Gudden, *Ergebn. exakt. Naturw.* **13**, 246 (1934); J. H. de Boer and W. Ch. van Geel, *Physica*, **2**, 286 (1935).

‡ Cf. C. Tubandt, *Handbuch der Experimentalphysik*, **12**, 1, p. 393, Leipzig (1932).

§ C. Wagner, *Z. phys. Chem. B*, **21**, 42 (1933); C. Tubandt and H. Reinhold, *Z. phys. Chem. B*, **24**, 22 (1934).

|| K. Baedeker, *Ann. Phys., Lpz.*, **22**, 756 (1907); **29**, 566 (1909).

by the taking up of an excess of halogen.\* It was shown by Tubandt and his collaborators† that in these cases also the conduction is of electronic nature.

Other electronegative elements such as sulphur and oxygen may also, when added in excess to certain sulphides or oxides, very much increase the conductivity of these substances. Thus the conductivity of  $\text{Cu}_2\text{S}$  is strongly increased by the taking up of sulphur; the conductivity of  $\text{Ag}_2\text{S}$ , however, becomes much smaller after the taking up of sulphur‡ as it is due to an excess of silver, which decreases with the taking up of sulphur. This phenomenon was first observed in the case of oxygen by le Blanc and Sachse§ in the taking up of this element by  $\text{NiO}$ . If 5 per cent. of oxygen is taken up in nickel oxide the conductivity becomes  $10^5$  times as high. Also with other oxides such as those of manganese, cobalt, copper, silver, gold, palladium, etc. one finds the same behaviour.||

The influence on the conductivity of cuprous oxide ( $\text{Cu}_2\text{O}$ ) by the taking up of oxygen has been especially thoroughly studied by various investigators.¶ Depending upon the oxygen content, values between  $10^{-2}$  and  $10^{-6}$  ohm $^{-1}$  cm. $^{-1}$  are found for the specific conductivity.

According to Wagner\*\* one may picture the mechanism of the strong electronic conduction caused by electronegative elements in the following manner. The excess electronegative element in the lattice forms excess negative ions, so that just as many of the positive ions must carry a higher charge. Let us take as an example cuprous iodide ( $\text{CuI}$ ) which has taken up a

\* C. Tubandt, *Z. anorg. Chem.* **110**, 234 (1920).

† C. Tubandt, E. Rindtorff and W. Jost, *Z. anorg. Chem.* **165**, 195 (1927); C. Tubandt, *Handbuch der Experimentalphysik*, **12**, 1, p. 446, Leipzig (1932).

‡ C. Tubandt and H. Reinhold, *Z. phys. Chem.* (1931); *Bodenstein Festband*, p. 874; *Z. Elektrochem.* **37**, 589 (1931).

§ M. le Blanc and H. Sachse, *Ber. sächs. Ges. (Akad.) Wiss.* **82**, 133 (1930).

|| M. le Blanc and H. Sachse, *Ber. sächs. Ges. (Akad.) Wiss.* **82**, 153 (1930); *Ann. Phys., Lpz.*, **11**, 727 (1931); *Phys. Z.* **32**, 887 (1931).

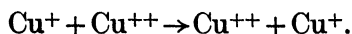
¶ O. v. Auwers, *Wiss. Veröff. Siemens-Konz.* **9**, 294 (1930); *Naturwissenschaften*, **19**, 133 (1931); B. Gudden and G. Mönch, *Naturwissenschaften*, **19**, 361 (1931); W. Vogt, *Ann. Phys., Lpz.* (5), **7**, 183 (1930); W. P. Jusé and B. W. Kurtschatow, *Phys. Z. Sowjet.* **2**, 453 (1932).

\*\* C. Wagner, *Phys. Z.* **32**, 641 (1931).

slight excess of iodine. Because of this taking up of iodine extra  $I^-$  ions are created in the lattice and an equally large number of  $Cu^{++}$  ions:



These  $Cu^{++}$  ions are those which bring about the electronic conduction, they are one electron short and can now capture an electron coming from a  $Cu^+$  ion, which is thereby in turn transformed into a  $Cu^{++}$  ion:



If we compare this scheme with the one which we found in § 81 for the electronic conduction in atomic coloured alkali halides, we see that, while with the alkali halides the conduction is caused by internally adsorbed atoms which emit their electrons, here the conduction is given by more highly charged ions which must capture an electron, thus by places where there is an electron missing. This sort of electronic conduction is therefore often called "defect conduction".

According to modern views the passage through the lattice of a place where there is one electron missing can be considered as if a charge carrier with a positive charge and about the mass of an electron were moving through the lattice. Connected with this view, according to Schottky and Waibel,\* is the fact that in the case of a defect conduction, in measurements in a magnetic field, a deflection of the charge carriers is found such as would be expected if they were positively charged (positive Hall constant). In the case of conduction due to "excess electrons" instead of missing electrons, one obtains a normal negative Hall effect. Thus  $CuI$  gives a positive Hall effect,  $MoS_2$  and  $Ag_2S$  negative ones.

We shall not go further into the phenomena of semi-conduction caused by electrons which are already freed by the thermal motion at room temperature, after having mentioned that, according to the systematic research of le Blanc and Sachse,† strong electronic conduction in oxides is found either when a portion of the valence electrons is not used in the chemical bond (lower oxides), or when by the taking up of an excess of oxygen metal ions of higher charge are formed. The

\* W. Schottky and F. Waibel, *Phys. Z.* **34**, 858 (1933).

† M. le Blanc and H. Sachse, *Phys. Z.* **32**, 887 (1931).

conductivity of  $\text{Cu}_2\text{O}$  is increased by an excess of oxygen as well as by an excess of copper\* (too strongly reduced  $\text{Cu}_2\text{O}$ , for example).

The photoelectric conductivity of cuprous oxide and the influence upon it of the taking up of oxygen have been investigated by Schönwald.† Besides the maximum of the photoelectric conduction at  $0.63\mu$  mentioned in § 89 which is connected with the long-wave extension of the absorption band of the lattice, and a maximum often occurring at  $0.8\mu$  which is ascribed to an impurity, perhaps copper, there is still a third region of photoelectric conduction. This last long-wave spectral region in which photoelectric conduction is found has a maximum at  $1.7\mu$  and extends further to about  $4\mu$  (0.3 electron volt). This region is connected with the excess oxygen taken up.‡ It must be noted that  $Q$  in the formula of thermal conductivity (the ordinary semi-conduction) can be calculated from the dependence of this conductivity on temperature in the case of the easily conducting, oxygen-containing preparations, and a value of about 0.25 electron volt is found. Similar values, around 0.3 electron volt, are found by Vogt§ and by Engelhard.|| According to the investigations of Jusé and Kurtschatow¶ the value of  $Q$  depends on the amount of oxygen taken up by the oxide. Preparations of  $\text{Cu}_2\text{O}$  with high amounts of extra oxygen give very low values of  $Q$  (0.13 electron volt).\*\* Here again, as in the case of  $\text{MoS}_2$  (§ 90), the energy necessary to obtain thermal ionization is smaller than the energy necessary for photoionization.

\* M. le Blanc and H. Sachse, *Ann. Phys., Lpz.*, **11**, 727 (1931); M. le Blanc, H. Sachse and H. Schöpel, *Ann. Phys., Lpz.*, **17**, 334 (1933).

† B. Schönwald, *Ann. Phys., Lpz.*, **15**, 395 (1932).

‡ B. Gudden, *Phys. Z.* **32**, 831 (1931).

§ W. Vogt, *Ann. Phys., Lpz.*, **7**, 183 (1930).

|| E. Engelhard, *Ann. Phys., Lpz.*, **17**, 501 (1933).

¶ W. P. Jusé and B. W. Kurtschatow, *Phys. Z. Sowjet.* **2**, 453 (1932).

\*\* In some cases ( $\text{CuI}$ ) a large amount of extra electronegative element leads to a zero value of  $Q$ ; the conductivity then decreases at higher temperatures, as does the conductivity of metals. The same is true for some semi-conductors which are provided with an extra amount of electropositive element ( $\text{Ag}_2\text{S}$ ). In these cases electrons are bound at "Lockerstellen", having energy values equal to that of the permitted empty band in the lattice. Cf. J. H. de Boer, *Chem. Weekblad*, **32**, 106 (1935).

## CHAPTER XIII

### PHOTOELECTRIC CATHODES WITH THICK INTERMEDIATE LAYERS CONSISTING OF A DIELECTRIC AND METAL PARTICLES

#### § 92. Photoelectric cathodes with thick intermediate layers of a dielectric.

In Chap. ix photoelectric cathodes were described which are made up in the following manner. A layer of some dielectric, upon whose surface alkali metal or alkaline earth metal atoms are adsorbed, is built up on a supporting metal. Upon absorption of light the adsorbed atoms are ionized, the electrons liberated are emitted as photoelectrons, and the positive ions remain adsorbed on the surface. In order that a photoelectric current shall continue to flow, these positive ions formed must be continually neutralized again, in other words there must be electrons supplied from within. The supplementary electrons have their source in the conduction electrons of the supporting metal and move through the dielectric intermediate layer to the positive ions formed by the photoionization. In the case of very thin, often monomolecular fluoride (§ 65), hydride (§ 66) or oxide (§§ 67 and 78) layers which were discussed in Chap. ix there is no difficulty about the electron flow; the electric fields of the ions are strong enough to draw electrons from the metal surface.

When, however, the layers of the dielectrics upon which the photosensitive atoms are adsorbed are made thicker, for example when they consist of layers of a hundred to five hundred molecules, serious difficulties arise in the supplementation of the emitted electrons. There is, however, reason to make the dielectric layers thicker, since with thick layers the number of active spots on the surface increases very much. This is very important since the photoelectrically active atoms are adsorbed on these active spots of the surface and thus, if the most favourable degree of occupation is chosen (§ 65), the photoelectric sensitivity will increase proportionally to the

number of active spots on the surface. The nature of the active spots may also be changed under certain circumstances, as appears from the difference between the [Ag]-Cs<sub>2</sub>O-Cs cathode in § 68 with a monomolecular Cs<sub>2</sub>O layer, and the same cathode with a Cs<sub>2</sub>O layer of several molecules thickness.\* The maximum of the spectral sensitivity of these cathodes lies at about 610 m $\mu$ , the photoelectric threshold at 900 m $\mu$ , when the Cs<sub>2</sub>O film is monomolecular, and between 1000 m $\mu$  and 1200 m $\mu$  when this film is several molecules thick. With a film of several molecules thickness there are not only more active spots on the surface, but especially are there active spots which exert a stronger electric field upon the adsorbed atoms and especially upon the adsorbed positive ions than with a monomolecular Cs<sub>2</sub>O film. The result of this is a photoionization of these adsorbed atoms at longer wave-lengths, and thus a shift of the photoelectric threshold toward longer wave-lengths.

With still thicker layers of the dielectric intermediate substance one may therefore expect higher photoelectric sensitivities, and perhaps also a shift of the photoelectric threshold toward longer wave-lengths if it is possible to increase the activity of the active spots. We shall see in the following sections that this expectation is actually fulfilled, when care is taken that the supplementation of electrons can take place unhindered through the dielectric layers.

If, however, no measures are taken to promote the supplementation of electrons, then the photoelectric sensitivity of the whole cathode as such decreases in spite of the increased number of active spots, when the intermediate layer becomes too thick. A characteristic of cathodes with dielectric intermediate layers which are too thick and therefore hinder the flow of electrons may be found in the lack of saturation. With too thick BaF<sub>2</sub> intermediate layers as well as with those of Cs<sub>2</sub>O layers cases have been observed where the photocurrent even with a tension of 200 volts between anode and cathode has shown no sign of saturation.†

\* J. H. de Boer and M. C. Teves, *Z. Phys.* **65**, 489 (1930).

† J. H. de Boer and M. C. Teves, *Z. Phys.* **74**, 605 (1932).

### § 93. Methods of preparing mixed intermediate layers (metal + dielectric).

The supplementation of electrons through the dielectric intermediate layers can be improved by building into these layers metal atoms or particles. In the foregoing chapters (X, XI and XII) we saw that the electronic conduction (the photoelectric as well as the thermal electronic conduction) of salt lattices can be noticeably improved by the introduction of internally adsorbed metal atoms or colloidal particles of metal.

It is possible to introduce such metal atoms or particles into the dielectric layer of the photoelectric cathode in several very different ways. If the dielectric layer is deposited by evaporation in a high vacuum, one can prepare such mixed layers as desired by simultaneous evaporation of metals and salts.

Evaporation processes with which a chemical decomposition is connected often lead to the desired goal.\* By heating a mixture of barium fluoride ( $\text{BaF}_2$ ) and tungsten powder in a high vacuum, a double decomposition takes place giving barium and a tungsten fluoride, both of which evaporate. Upon the wall where the products are deposited the reaction proceeds in the opposite direction, so that as a result a layer is obtained, which consists of barium fluoride and tungsten thoroughly mixed. The evaporation of a mixture of barium fluoride, silica and tungsten powder gives layers which consist of an intimate mixture of barium fluoride, silicon, tungsten oxide and tungsten. By evaporation of a mixture of magnesium oxide and tungsten a layer is formed which again consists of an intimate mixture of the two substances. With other metals, for example molybdenum, zirconium, iron, etc., one can also carry out similar reactions with metal oxides or metal halides.

One also obtains mixed layers by allowing alkali or alkaline earth metals to react upon the halides or oxides of heavy metals (§ 12). Thus by the reaction of caesium on a silver oxide layer, when the temperature is not too high (in general below  $200^\circ \text{C.}$ ), a caesium oxide ( $\text{Cs}_2\text{O}$ ) layer is formed with which the silver resulting, probably in atomic form, and in any case

\* J. H. de Boer and M. C. Teves, *Z. Phys.* **74**, 607 (1932).

very finely dispersed, is intimately mixed.\* These layers are coloured yellow to brown.

Further, one may deposit a layer of some metal by sublimation upon an already formed dielectric layer or even upon a finished photoelectric cathode, and thereafter provide for mixture by diffusion by means of heating. In this manner Asao and Suzuki† added extra silver particles or gold particles to mixed layers consisting of an alkali oxide and silver, while Sewig‡ introduced still other metals into the layer in this way.

Layers which consist of alkali oxides and silver, but which contain more silver particles than the layer obtained by decomposition of silver oxide ( $\text{Ag}_2\text{O}$ ) by an alkali metal, may also be prepared by starting with a layer consisting of silver oxide and silver. If silver is first oxidized and then partially reduced, which can be done with hydrogen for instance, one obtains a layer consisting of silver oxide and silver; by reduction with an alkali metal an alkali oxide layer is formed with excess silver particles.§

The electron conduction through the dielectric intermediate layer is facilitated by the building into the layer of atoms or particles of a photoelectrically active metal. This can be done by heating the intermediate layer in the vapour of an alkali metal, thus by the additive method of coloration, discussed in detail in §§ 75 and 82. The fact that a calcium fluoride layer after being heated in caesium vapour showed photoelectric conductivity proves that an intermediate layer can thereby be made photoelectrically conductive. While we formerly assumed|| that here caesium had penetrated into the calcium fluoride lattice, we must now, due to the experiments mentioned in § 82, accept the view that the photoelectric conduction is caused by calcium atoms which have been formed in the lattice during the heating in caesium vapour (see § 82).

\* N. R. Campbell, *Phil. Mag.* **12**, 174 (1931); J. H. de Boer and M. C. Teves, *Z. Phys.* **74**, 609 (1932).

† S. Asao and M. Suzuki, *Proc. phys.-math. Soc. Japan* (3), **12**, 247 (1930).

‡ R. Sewig, *Z. Phys.* **76**, 91 (1932).

§ M. C. Teves and J. H. de Boer, will appear shortly in *Physica*.

|| J. H. de Boer and M. C. Teves, *Z. Phys.* **74**, 607 (1932).



This method of obtaining photoelectric conduction by heating in the vapour of an alkali metal proceeds much more easily when other foreign atoms are already present. Because of the foreign atoms there are of course many more internal surfaces and places of disturbance, upon which an internally adsorbed alkali or alkaline earth atom can find a place. Not only does the possible number of internally adsorbed atoms increase very much when foreign atoms are present, but the complete occupation of these places of disturbance by alkali or alkaline earth metal atoms is also favourable for the conduction, since the distances over which the electrons can move in the lattice before they are recaptured become greater. This last point is quite analogous to what we saw in § 87, viz. that the distances covered by electrons in coloured silver halide are much greater than when the places of disturbance are not occupied by atoms.

Caesium atoms can be introduced much more easily into the interior of a caesium oxide layer when silver atoms or particles are present. This "penetration" can be brought about already at 100° C.; heating in caesium vapour at a temperature between 170 and 200° C. gives more quickly the desired result. Görlich\* introduces caesium atoms into the layer by heating it at 160 to 180° C. and shooting caesium ions into it at the same time.

**§ 94. Photocathodes with mixed metal-salt layers, especially the [Ag]-Cs<sub>2</sub>O, Ag-Cs cathode.**

As was stated in § 92, one of the evidences of an insufficient supplementation of electrons through the dielectric intermediate layer is a lack of saturation of the photocurrent. Saturation currents are much more easily obtained with intermediate layers in which metal atoms or particles are built in. In Fig. 134 a current-tension curve is given for a barium fluoride layer without atoms built in, and one for a barium fluoride layer in which tungsten atoms and also internally adsorbed barium atoms are introduced, on both of which layers caesium atoms are adsorbed. One can see that with the

\* P. Görlich, *Z. Phys.* **85**, 128 (1933).

mixed layer a practically saturated photocurrent is obtained at 30 to 40 volts. In addition the photocurrents measured in white light are greater with mixed layers (about double with barium fluoride) than with the use of an equally thick layer of the pure dielectric alone.\*

Various investigators have in recent years published results of the photoelectric emission of photocathodes where an alkali metal, usually caesium, is adsorbed upon a mixed layer of alkali oxide (caesium oxide) and silver. This layer is obtained

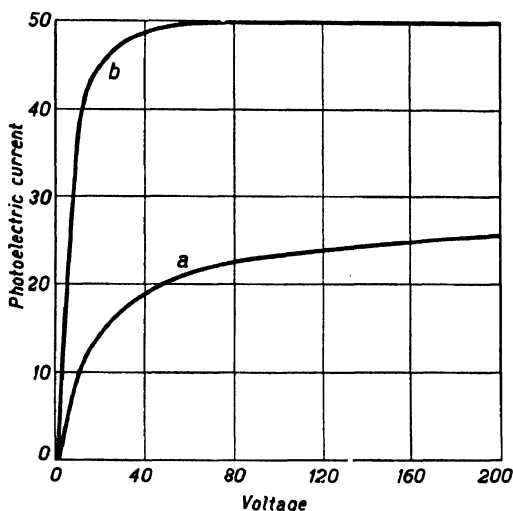


Fig. 134. Photoelectric current as a function of the tension: *a*, Cs atoms on a pure BaF<sub>2</sub> layer; *b*, Cs atoms on a BaF<sub>2</sub> layer, mixed with tungsten and barium.

in most cases, as was mentioned in § 93, by allowing the alkali metal to react with silver oxide.

Thus for example Koller† oxidizes the surface of a silver layer in such a way as to give a layer of silver oxide several hundred molecules thick. If caesium is admitted afterwards, it is completely absorbed by the silver oxide. The system is then heated (to 250°C.) and a reaction takes place between the silver oxide and the caesium giving caesium oxide and silver. Since some of the excess caesium is adsorbed on the surface of the layer formed, a photoelectrically sensitive

\* J. H. de Boer and M. C. Teves, *Z. Phys.* **74**, 609 (1932).

† L. R. Koller, *Phys. Rev.* **36**, 1641 (1930).

layer is obtained which has quite different properties from the  $[\text{Ag}]\text{-O,Cs}$  cathodes also studied by Koller or from the  $[\text{Ag}]\text{-Cs}_2\text{O-Cs}$  cathode described in § 68. The spectral sensitivity is represented in Fig. 135,\* from which it can be seen that a maximum of the sensitivity is found at about  $750\text{m}\mu$  and another at  $350\text{m}\mu$ . This photoelectric cathode differs very much, especially in regard to the long-wave maximum, from the  $[\text{Ag}]\text{-O,Cs}$  cathode (Fig. 92 in § 68), which only gives a maximum at  $350\text{m}\mu$ , and also from the  $[\text{Ag}]\text{-Cs}_2\text{O-Cs}$  cathodes

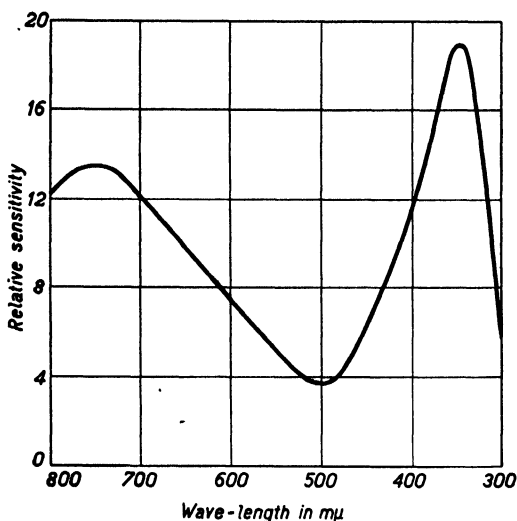


Fig. 135. Spectral distribution of photoelectric sensitivity of a  $[\text{Ag}]\text{-Cs}_2\text{O}$ ,  $\text{Ag-Cs}$  cathode. L. R. Koller, *Phys. Rev.* **36**, 1642 (1930).

(Figs. 90 and 91 in § 68), which have a maximum at  $610\text{m}\mu$ . Instead of the symbol  $\text{Cs-CsO-Ag}$  used by Koller, we shall represent this new cathode, which has an intermediate layer consisting of  $\text{Cs}_2\text{O}$  and  $\text{Ag}$ , by the symbol  $[\text{Ag}]\text{-Cs}_2\text{O,Ag-Cs}$ .

It must be noted that Campbell and Ritchie† describe a photoelectric cathode which is evidently formed by adsorption of a thin film of caesium on oxidized silver, without a reaction of the caesium with the silver oxide having been performed.

\* Cf. L. R. Koller, *J. West. Soc. Engrs*, **36**, 15 (1931).

† N. R. Campbell and D. Ritchie, *Photoelectric Cells*, London, Sir Isaac Pitman and Sons, p. 36 (1929).

This cathode also has a maximum of the spectral sensitivity at  $750\text{ m}\mu$ ; the spectral sensitivity decreases toward shorter wave-lengths, and the maximum at  $350\text{ m}\mu$  (or around  $400\text{ m}\mu$ ) which is characteristic of the  $[\text{Ag}]-\text{Cs}_2\text{O}$ ,  $\text{Ag}-\text{Cs}$  cathode is not present.

Campbell\* later also describes an intermediate layer which results from a chemical reaction between caesium and silver oxide (a layer of oxide at least ten molecules thick). The cathode prepared with this layer has a maximum of the sensitivity at  $700\text{ m}\mu$ .

Kelly† describes a photocathode in the form of a silver sheet upon which there is formed a matrix of caesium oxide, silver oxide and finely divided silver. Upon this matrix there is deposited a thin film of caesium. This cathode has a photoelectric threshold beyond  $1200\text{ m}\mu$  and a maximum of sensitivity at about  $800\text{ m}\mu$ . In a later publication Prescott and Kelly‡ describe the preparation of these cathodes whereby the intermediate layer is also obtained by reaction of caesium on silver oxide. The silver oxide is best obtained by a glow discharge in oxygen, as many other investigators also describe,§ where the silver surface to be superficially oxidized is the cathode. Prescott and Kelly examined among other things the influence of the amount of adsorbed caesium on the position of the long-wave maximum in the spectral sensitivity of these cathodes. Fig. 136 gives several of their curves. With increasing amount of adsorbed caesium the maximum rises and is shifted toward longer wave-lengths (curves 1 and 2); at about  $800\text{ m}\mu$  an optimum of the long-wave excursion of the maximum is found, while at the same time the photoelectric threshold is shifted as far as possible toward long wave-lengths. If the amount of caesium adsorbed still increases, the maximum will rise but is shifted back toward shorter wave-lengths, and the photoelectric threshold is also shifted back (curve 3). If still more caesium is added the maximum falls and is at the

\* N. R. Campbell in *Photoelectric Cells and their Applications*, J. S. Anderson, London, p. 10 (1930).

† M. J. Kelly, *J. Soc. Mot. Pict. Engrs*, **18**, 761 (1932).

‡ C. H. Prescott Jr. and M. J. Kelly, *Bell Syst. Tech. J.* **11**, 334 (1932).

§ Cf. N. R. Campbell, *Phil. Mag.* **12**, 173 (1931); J. H. de Boer and M. C. Teves, *Z. Phys.* **74**, 604 (1932); W. Kluge, *Phys. Z.* **34**, 115 (1933).

same time shifted toward shorter wave-lengths; the photoelectric threshold is also further withdrawn (curve 4).

From the above statements it appears that the position of the long-wave maximum varies with the  $[\text{Ag}]\text{-Cs}_2\text{O}$ ,  $\text{Ag-Cs}$  cathodes between 700 and 800  $m\mu$ . Detailed research by Kluge\* throws new light upon the meaning of the short-wave maximum of these cathodes. He examined not only the  $[\text{Ag}]\text{-Cs}_2\text{O}$ ,  $\text{Ag-Cs}$  cathode, but also combinations built up of

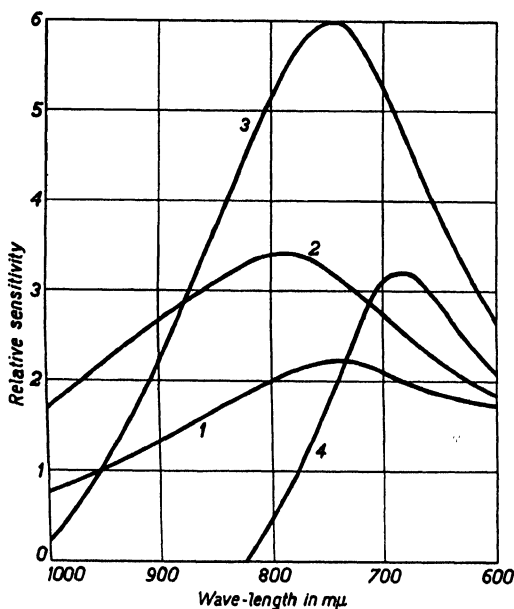


Fig. 136. Several spectral distribution curves of  $[\text{Ag}]\text{-Cs}_2\text{O}$ ,  $\text{Ag-Cs}$  photocathodes with different amounts of adsorbed Cs atoms. The amount of Cs increases from curve 1 to curve 4. C. H. Prescott, Jr. and M. J. Kelly, *Bell Syst. Tech. J.* 11, 334 (1932).

other alkali metals and their oxides. While the position of the long-wave maximum is very dependent upon the alkali metal used, the short-wave maximum is in all these cases situated at practically the same wave-length. In Fig. 137 several of the spectral distribution curves obtained by Kluge are reproduced and they demonstrate the above statement very clearly. With the  $[\text{Ag}]\text{-Na}_2\text{O}$ ,  $\text{Ag-Na}$  cathodes the long-wave maximum can no longer be distinguished individually; it falls within the

\* W. Kluge, *Phys. Z.* 34, 115 (1933).

region of the short-wave maximum. Table XI gives some data relating to these cathodes.

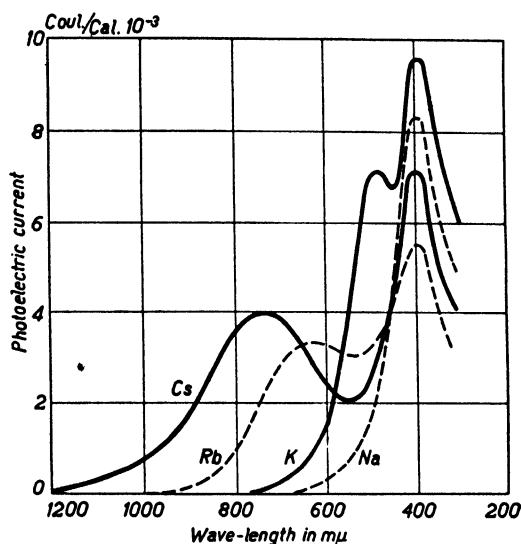


Fig. 137. Spectral distribution of  $[\text{Ag}]\text{-Me}_2\text{O, Ag-Me}$  cathodes ( $\text{Me} = \text{Cs, Rb, K or Na}$ ). W. Kluge, *Phys. Z.* **34**, 115 (1933).

Table XI

Data relating to  $[\text{Ag}]\text{-Me}_2\text{O, Ag-Me}$  cathodes  
(W. Kluge, *Phys. Z.* **34**, 125 (1933)).

Cathode	Short-wave maximum $\text{m}\mu$	Long-wave maximum $\text{m}\mu$	Long-wave limit $\text{m}\mu$	Energy of the $h\nu$ of the long- wave limit electron volts
$[\text{Ag}]\text{-Na}_2\text{O, Ag-Na}$	410–420	*	$\sim 680$	$\sim 1.85$
$[\text{Ag}]\text{-K}_2\text{O, Ag-K}$	400–420	460–520	$\sim 800$	$\sim 1.55$
$[\text{Ag}]\text{-Rb}_2\text{O, Ag-Rb}$	400–420	620–680	$\sim 1000$	$\sim 1.2$
$[\text{Ag}]\text{-Cs}_2\text{O, Ag-Cs}$	410–430	730–800	$\sim 1200$	$\sim 1.0$

It was assumed by Kluge the long-wave maxima must be ascribed to the alkali metal used, but that the short-wave maxima are connected with the silver. By means of a detailed examination using polarized light he† was able to confirm that the long-wave maxima must be considered as photo-ionization bands of the adsorbed alkali metal atoms (cf. § 71).

\* Not observable

† W. Kluge, *Phys. Z.* **34**, 465 (1933).

The supposition that the short-wave maxima, which according to Table XI lie at about  $410\text{ m}\mu$  on the average, are connected with the silver and more especially with the silver built into the layer, was rendered probable by later research of Kluge.\* It must be noted that the position of the short-wave maximum given in Table XI does not agree with its position ( $350\text{ m}\mu$ ) as found by Koller (see above). Kluge found two maxima in

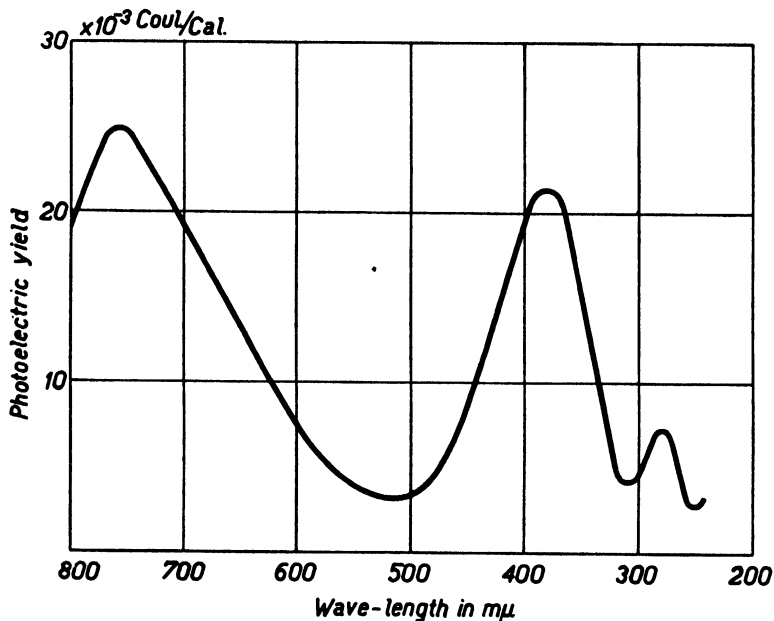


Fig. 138. Spectral distribution of photoelectric sensitivity of a  $[\text{Ag}]\text{-Cs}_2\text{O}$ ,  $\text{Ag-Cs}$  cathode. R. Fleischer and P. Görlich, *Phys. Z.* **35**, 291 (1934).

a more detailed examination, one at  $370\text{ m}\mu$  and one at  $290\text{ m}\mu$ . If oxygen is admitted to the cathode the adsorbed caesium is oxidized and the long-wave maximum seems to disappear entirely. A photocathode remains which has a threshold at  $460\text{ m}\mu$  and which has still kept the two above-mentioned short-wave maxima unchanged at  $370\text{ m}\mu$  and  $290\text{ m}\mu$ , although they are decreased in height.† In the case of other metals also,

\* W. Kluge, *Phys. Z.* **34**, 844 (1933).

† According to an unpublished investigation by M. C. Teves these maxima also disappear, provided one waits long enough after the admission of the oxygen. In a very recent publication, Kluge, *Z. Phys.* **93**, 636 (1935), states that these maxima are not connected with the silver.

such as copper, nickel and gold, Kluge has found two corresponding maxima. These two short-wave maxima were confirmed by Fleischer and Görlich,\* who gave as wave-lengths  $375\text{ m}\mu$  and  $280\text{ m}\mu$  (Fig. 138).

§ 95. [Ag]-Cs<sub>2</sub>O, Ag-Cs cathodes with excess metal particles in the intermediate layers, and [Ag]-Cs<sub>2</sub>O, Cs, Ag-Cs cathodes.

As was mentioned in § 93 Asao and Suzuki† introduce excess silver or gold particles on the [Ag]-Cs<sub>2</sub>O, Ag-Cs cathode by sublimation, whereafter upon reheating the cathode they

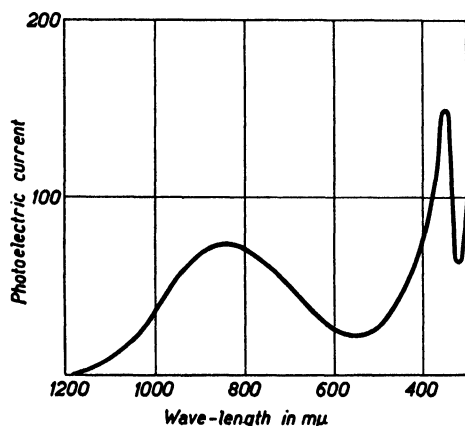


Fig. 139. Representative spectral distribution curve of a [Ag]-Cs<sub>2</sub>O, Ag-Cs cathode with a surplus of Ag in the layer. S. Asao, *Physics*, 2, 19 (1932).

obtain a greater sensitivity for white light. Spectral distributions of the photoelectric sensitivity of such cathodes with excess silver particles are described later by Asao.‡ The long-wave maximum is in general displaced somewhat toward longer wave-lengths, so that the maximum is sometimes at greater wave-lengths than  $800\text{ m}\mu$  (Fig. 139). Similar results were found using potassium and rubidium in the place of caesium, when excess silver was evaporated and the cathode then heated.

Sewig§ introduced many other metal particles in excess into

\* R. Fleischer and P. Görlich, *Phys. Z.* 35, 289 (1934).

† S. Asao and M. Suzuki, *Proc. phys.-math. Soc. Japan* (3), 12, 247 (1930).

‡ S. Asao, *Physics*, 2, 12 (1932).

§ R. Sewig, *Z. Phys.* 76, 91 (1932).



the intermediate layers of  $[\text{Ag}]\text{-Cs}_2\text{O}$ ,  $\text{Ag-Cs}$  cathodes by the same method (evaporation, and heating to promote diffusion). All the metals examined (Ta, Mo, Fe, W, Pt, Ni, Cu, Au) gave an increase of the total sensitivity for white light; Ni, W and Ta were especially favourable. The photoelectric threshold is scarcely influenced by the treatment. It is remarkable that Sewig gives a pronounced extra maximum in his curves at about  $520\text{ m}\mu$ , which was never found by other investigators of such caesium cathodes.

One arrives at similar intermediate layers if excess metal particles are added to the oxide to be reduced before its reaction with the alkali metal. This can be done, for instance, by first oxidizing the silver surface as cathode in a glow discharge in oxygen, until a relatively thick layer of oxide is obtained (several hundred molecules), and then partially reducing this  $\text{Ag}_2\text{O}$  again.\*

This silver oxide can be reduced quantitatively by hydrogen at room temperature in a slow reaction; a partial reduction of 10 to 20 per cent. (at about  $150^\circ\text{C}$ . for a short time), however, gives a mixture of  $\text{Ag}_2\text{O}$  and silver, which upon its subsequent reaction with caesium produces a mixed intermediate layer of  $\text{Cs}_2\text{O}$  and excess silver particles. One arrives also at such intermediate layers if after the oxidation a layer of silver (or other metal) is first evaporated upon the silver oxide, and then the alkali metal, caesium for example, is allowed to react.

In general one gets the impression that the total sensitivity is raised by the building in of excess metal particles, and that the maximum of the photoelectric sensitivity is shifted toward longer wave-lengths; the photoelectric threshold on the other hand remains at about  $1200\text{ m}\mu$ . A displacement of the photoelectric threshold is obtained if extra atoms of the photoelectrically active alkali metal adsorbed on the outside surface are also adsorbed internally in the intermediate layer.† In order to accomplish this in the case of the alkali oxide inter-

\* J. H. de Boer and M. C. Teves, will appear shortly in *Rec. Trav. chim. Pays-Bas*.

† J. H. de Boer and M. C. Teves, *Z. Phys.* **74**, 604 (1932).

mediate layers, the silver oxide layers obtained by cathodic oxidation in a glow discharge are very suitable. These layers, thanks to their method of formation, have a very porous structure which makes them comparable to the salt films obtained by sublimation (§ 59). In the cathodic oxidation the silver oxide is also formed in the gaseous phase and then again deposited, so that this structure is quite understandable.\*

In the reaction with caesium to give caesium oxide and silver a number of internally adsorbed caesium atoms can be introduced by heating for some time in caesium vapour (cf. §§ 75 and 82). This is done by heating the whole apparatus with an excess of caesium for some time at a temperature below  $200^{\circ}\text{C}$ .† By this building in of caesium atoms the total sensitivity for white light is also raised very much; a direct comparison, in which one cell was provided with caesium atoms built into the intermediate layer and one was not, gave as result that the photocathode with caesium atoms built in had a total sensitivity about twice as great as the photocathode which was not provided with extra caesium atoms.‡ The maximum of the spectral sensitivity is also somewhat shifted by this building in of caesium atoms toward longer wavelengths, but especially the photoelectric threshold is shifted. Evidently under this treatment some caesium atoms are added whose photoionization proceeds more easily with respect to energy, at least the curve of the spectral sensitivity exhibits in this case a long-wave extension beyond  $1200\text{m}\mu$  which extends to  $1400\text{m}\mu$ § (Fig. 140). We may indicate these cathodes by the symbol  $[\text{Ag}]\text{-Cs}_2\text{O,Cs,Ag-Cs}$ .

A somewhat different method of making these cathodes is followed by Görlich|| (cf. § 93), when he allows caesium ions to penetrate into the layer. His results confirm the above very well.

\* J. H. de Boer and M. C. Teves, will appear shortly in *Rec. Trav. chim. Pays-Bas*.

† Cf. also N. R. Campbell, *Phil. Mag.* **12**, 173 (1931).

‡ J. H. de Boer and M. C. Teves, *Z. Phys.* **83**, 521 (1933).

§ J. H. de Boer and M. C. Teves, *Z. Phys.* **74**, 611 (1932) (cf. Fig. 139).

|| P. Görlich, *Z. Phys.* **85**, 128 (1933).

A still greater shift toward longer wave-lengths of the maximum of the spectral sensitivity as well as of the photoelectric threshold is obtained if once more excess silver particles (or particles of another metal) are added to these  $[\text{Ag}]\text{-Cs}_2\text{O}$ ,  $\text{Cs,Ag-Cs}$  cathodes. This can be carried out either by sublimating the metal after the formation of the cathode, and again subjecting the cathode to a temperature treatment,\* or by starting with a silver oxide layer with excess silver

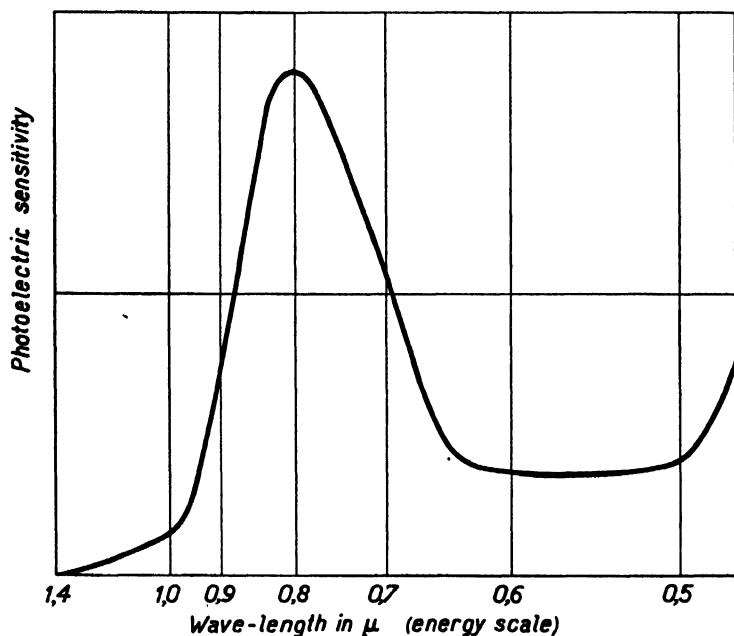


Fig. 140. Spectral distribution curve of a  $[\text{Ag}]\text{-Cs}_2\text{O,Cs,Ag-Cs}$  cathode.

atoms for the reaction of caesium on silver oxide.† The result is that photocathodes are obtained whereby the maximum of the spectral sensitivity may have been shifted to  $850\text{ m}\mu$ , while other cases are known in which the long-wave extension of the spectral sensitivity extends to  $1700\text{ m}\mu$ .

If we compare finally the various photoelectric cathodes which may be formed of combinations of silver, oxygen and caesium, we obtain the results presented in Table XII.†

\* R. Fleischer and P. Görlich, *Phys. Z.* 35, 289 (1934).

† M. C. Teves and J. H. de Boer, will appear shortly in *Physica*.

Table XII

Cathode	Photoelectric threshold in $m\mu$	Maximum at longest wave-length in $m\mu$
[Ag]-O,Cs	800	350
[Ag]-Cs <sub>2</sub> O-Cs	$\sim 1150^*$	610
[Ag]-Cs <sub>2</sub> O,Ag-Cs	$\sim 1200$	700 to 800
[Ag]-Cs <sub>2</sub> O,Ag-Cs with extra Ag(Me)	$\sim 1200$	750 to above 800
[Ag]-Cs <sub>2</sub> O,Cs,Ag-Cs	to $\sim 1400$	750 to above 800
[Ag]-Cs <sub>2</sub> O,Cs,Ag-Cs with extra Ag(Me)	to $\sim 1700$	750 to 850

### § 96. The phenomenon of excitation in the supplementation of electrons, and its consequences.

With the [Ag]-Cs<sub>2</sub>O,Cs,Ag-Cs cathodes which were treated in the previous section various phenomena were observed,† which are connected with the excitation with which we became acquainted in § 77. When, during the supplementation of electrons through the intermediate layer, some electrons remain fixed upon internal surfaces or places of disturbance, a corresponding number of positive ions remains unneutralized. Because of this the cathode is temporarily poorer in externally and internally adsorbed atoms, so that the sensitivity as a whole decreases. After a rather long illumination a decrease of the sensitivity is actually found, and it is stronger the greater the intensity of the light used. Besides this decrease of the sensitivity for white light which is manifested as a fatigue phenomenon, the spectral distribution of the sensitivity also changes, and the maximum is shifted somewhat, the photoelectric threshold quite noticeably, toward shorter wavelengths. This withdrawal of maximum and threshold (Fig. 141) is connected with the formation of a number of positive caesium ions on the surface and in the intermediate layer which are temporarily unneutralized. The presence of positive charges renders it more difficult in respect to energy to effect photo-ionization of the adsorbed atoms still present, a fact which follows immediately from the discussions in §§ 62, 65, 70 and 83.

\* 900  $m\mu$  with a monomolecular Cs<sub>2</sub>O intermediate layer, cf. § 68.

† J. H. de Boer and M. C. Teves, *Z. Phys.* **74**, 613 (1932).

The electrons which have remained fixed upon internal surfaces or places of disturbance form excitation centres (§ 77). The same means of neutralizing the excitation which we saw in §§ 77 and 87, viz. by passage of time (i.e. recovery by means of the thermal agitation at room temperature), by heating or by irradiation with red or infrared light, are here also useful for the recovery of the original sensitivity of the photocathode. A cathode whose sensitivity was decreased almost one-half

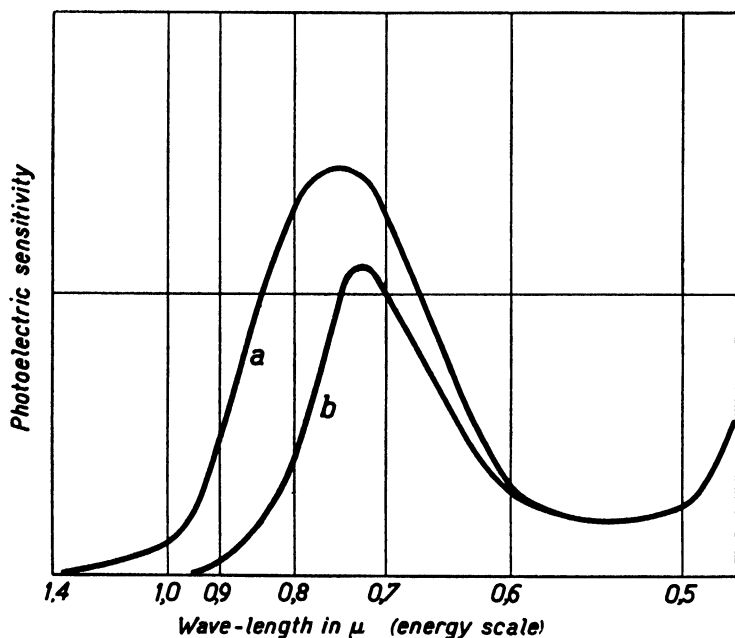


Fig. 141. Spectral distribution curve of a  $[\text{Ag}]\text{-Cs}_2\text{O, Cs, Ag-Cs}$  cathode: *a*, in a fresh state; *b*, after fatigue has set in.

by irradiation with white light for several hours, has, after having been kept in darkness for 24 hours at room temperature, practically recovered; a short heating for a few minutes at  $200^\circ\text{C}$ . also restores the cathode. By irradiation with infrared light the cathode recovers much more quickly than by simply being kept in the dark. The neutralization of the excitation by means of infrared light is so intense, that when the photocathode is used in infrared light no decrease of the sensitivity, i.e. no fatigue, is observed; with red light there is only a very slight decrease of the sensitivity with the time, with green or

blue light the decrease is very strong (Fig. 142). When by one of these three above-mentioned methods the cathode has been restored to its former sensitivity, the photoelectric threshold is again shifted to  $1400\text{ m}\mu$  and the maximum of the spectral sensitivity to longer wave-lengths.

The fatigue phenomena of the cathodes, which are the consequences of the above-described hindering of the electronic supplementation, are still more strengthened by a phenomenon electrolytic in nature. The positive caesium ions, which are constantly formed, are drawn toward the inside under the

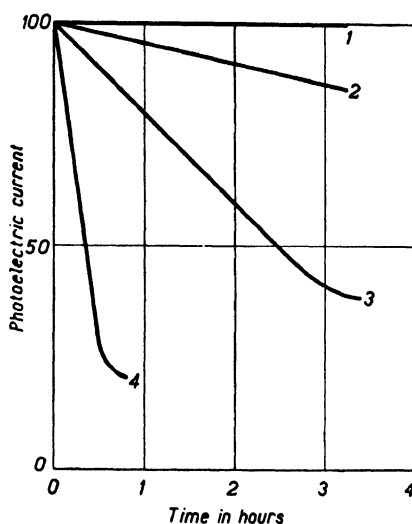


Fig. 142. Decrease of current for a given [Ag]-Cs<sub>2</sub>O,Cs,Ag-Cs cathode: 1, in infrared light; 2, in red light; 3, in green light; 4, in blue light.

influence of the applied tension between anode and cathode. The surface of the cathode thus becomes poorer in photoelectrically active atoms, so that the sensitivity also decreases. Since this electrolytic phenomenon is stronger according as the applied field is stronger, it is plain that the fatigue phenomena are more pronounced the higher the applied tension. The positive ions which are drawn toward the inside, are there neutralized and then diffuse again to the outside as neutral atoms.

The direct hindering of the electronic supplementation as well as the electrolytic impoverishment of the outside surface

which is a result of the former, are more pronounced at low temperatures than at higher temperatures. There are, however, indications that at  $-196^{\circ}\text{C}.$ , for instance, the electrolytic portion of the fatigue phenomena is of less importance than the direct electronic portion.\*

The fatigue effects due to the excitation phenomena are stronger according as the supplementation of electrons is more difficult. It will be quite plain here that, when the distances which can be covered by the electrons in the lattice are greater because of a building in of foreign metal atoms and especially caesium atoms, the excitation will be weaker. Good  $[\text{Ag}]\text{-Cs}_2\text{O}$ ,  $\text{Cs,Ag-Cs}$  cathodes with many excess silver particles, which allow many extra caesium atoms to be adsorbed internally, have a good saturation characteristic (§ 94) and also exhibit to the smallest degree the fatigue phenomena.†

Suhrmann and Dempster‡ have found fatigue phenomena in the case of a photoelectric cathode in which potassium atoms are adsorbed upon a naphthalene surface. These phenomena also are based upon a difficulty of the electronic supplementation since electrons remain stuck in the intermediate layer.

### § 97. The supplementation of electrons and the sensitivity of the photocathodes.

It will be quite plain from the discussion in the previous sections that the sensitivity of those cathodes, in which alkali or alkaline earth metal is adsorbed upon a thick dielectric intermediate layer, is closely connected with the greater or less ease with which the supplementation of electrons takes place. A clear example of this is offered by the photoelectric properties of cathodes in which barium atoms are adsorbed upon a relatively thick barium oxide film. As we shall see in the following chapter the thermionic, so-called "oxide", cathodes have such a structure (§ 101). It has long been known that the thin layers which are formed upon the anode of a thermionic tube by evaporation from the cathode can

\* J. H. de Boer and M. C. Teves, *Z. Phys.* 74, 620 (1932).

† M. C. Teves and J. H. de Boer, will appear shortly in *Physica*.

‡ R. Suhrmann and D. Dempster, *Phys. Z.* 35, 148 (1934).

themselves be used as photoelectric cathodes.\* These layers also consist of films of barium oxide, thin to be sure, upon which barium atoms are adsorbed. In the case of the "oxide cathode" itself the dielectric intermediate layer is much thicker, which makes, at least at room temperature, the supplementation of electrons more difficult still. Case† observed a photoelectric sensitivity with these cathodes. The photoelectric threshold of such a cathode lies at  $9200\text{\AA}$ . according to an investigation by Huxford.‡

At higher temperatures, especially at the temperatures at which these cathodes are used as thermionic cathodes, the electron conduction of the barium oxide intermediate layer is great enough to guarantee a sufficient supply for the photoelectric emission also. At higher temperatures the photoelectric emission is found to rise sharply.§ It is not probable that the total increase of the current measured due to illumination is to be ascribed to a direct primary photoelectric current (the increase of the current is approximately by a factor  $10^3$ ); according to an investigation of Ramadanoff,|| however, an increase to 16 times the direct photoelectric current by illumination with intermittent light can be observed at a high temperature. Unpublished measurements by M. C. Teves completely confirm this result. As a result of the much improved supplementation of electrons at a high temperature, a very great increase of the photoelectric sensitivity is noted in every case.

Another problem is whether the maximum of the spectral distribution curve of complex photocathodes is dependent

\* T. W. Case, *Phys. Rev.* **17**, 398 (1921); *Proc. Amer. electrochem. Soc.* **39**, 423 (1921); cf. also T. W. Case in J. S. Anderson, *Photoelectric Cells and their Applications*, p. 49, London (1930).

† T. W. Case, *Phys. Rev.* **17**, 398 (1921).

‡ W. S. Huxford, *Phys. Rev.* **37**, 102 (1931).

§ Cf. E. Merritt, *Phys. Rev.* **17**, 525 (1921); O. Koppings, *Phys. Rev.* **18**, 443 (1921); R. C. Gibbs and E. L. Meacham, *Phys. Rev.* **19**, 415 (1922); W. H. Crew, *Phys. Rev.* **28**, 1265 (1926); K. Newbury, *Phys. Rev.* **34**, 1418 (1929); C. E. Berger, *Phys. Rev.* **34**, 1566 (1929); K. Newbury and F. Lemery, *J. opt. Soc. Amer.* **21**, 276 (1931).

|| D. Ramadanoff, *Phys. Rev.* **37**, 884 (1931).



upon the supplementation of electrons through the intermediate layer. We have seen in Chaps. x and xi that only electrons with definite energies can move through a lattice (see especially § 85). If the electrons supplied are also mainly freed photoelectrically from the atoms adsorbed internally in the layer then the energy conditions of § 85 must hold here also. In § 85 we saw that in the case of the sodium chloride lattices the distance between two permitted energy bands in the lattice (the electrons move in the 110 direction) was given by the formula

$$\Delta E = \frac{h^2}{8md^2},$$

while the following holds experimentally for the absorption bands of the internally adsorbed alkali metal atoms in the alkali halides:\*

$$\nu d^2 = 0.50 \text{ cm.}^2/\text{sec.},$$

which gives approximately the relation†

$$h\nu = \frac{h^2}{16md^2}.$$

We saw in § 71 that Olpin,‡ expanding upon the theory of Fowler,§ derived the relation for the frequency of the maximum of the selective photoelectric emission

$$h\nu = \frac{h^2}{8md^2},$$

a relation thus completely analogous to that which holds for the photoelectric conduction. Because of this it is still possible, as was indicated in § 71, that, in spite of the invalidity of the premises of Fowler's theory, the formula derived from it is valid for the photoelectric cathodes with thick dielectric intermediate layers, since similar formulae hold for photoelectric conduction. If the supplementation of electrons is the dominating factor in the spectral distribution of the sensitivity, such a formula holds for the maximum of the spectral distribution.||

\* E. Mollwo, *Nachr. Ges. Wiss. Göttingen*, p. 97 (1931).

† H. Fröhlich, *Z. Phys.* **80**, 819 (1933).

‡ A. R. Olpin, *Phys. Rev.* **38**, 1745 (1931).

§ R. H. Fowler, *Proc. roy. Soc. A*, **128**, 123 (1930).

|| J. H. de Boer and M. C. Teves, *Z. Phys.* **83**, 530 (1933).

## CHAPTER XIV

# THERMIONIC EMISSION OF CATHODES WITH A DIELECTRIC; OXIDE- COATED CATHODES

### § 98. Introduction; the constants of the emission formula.

In § 79 we discussed the possibility of a thermal ionization of atoms adsorbed on a dielectric. In Chaps. XI and XII we became acquainted with many cases of electronic conduction in lattices of dielectrics, which conduction is a result of this thermal ionization of internally adsorbed atoms, whereby the electron is emitted within the lattice. We shall in this chapter discuss various cases in which the electrons freed by the thermal ionization of adsorbed atoms are emitted toward the outside, so that we are again concerned with the phenomena of thermionic emission and the influence of adsorbed atoms upon these phenomena.

There is, however, a great difference between the thermionic emission discussed in Chaps. III, IV and VI, and that which we shall here discuss. In the case of the thermionic emitting cathodes of Chaps. III, IV and VI, it was the conduction electrons of a metal which were emitted thermally, and the influence of the adsorbed atoms consisted in the fact that they increased or decreased the work function  $\phi$  according as the electric double layer formed by the adsorbed atoms had its negative side toward the outside or toward the inside. In all those cases the adsorbed atoms—of electropositive as well as of electronegative elements—were adsorbed directly upon the metal surface itself, so that they were either transformed into ions and then together with their mirror images formed dipoles, or were polarized as atoms. In this chapter, however, we shall discuss cases of thermionic emission where the electrons emitted are not, in the first place, the conduction electrons of a metal, but the valence electrons of adsorbed atoms which are detached by thermal ionization.

The thermionic emission with which we shall become acquainted in this chapter stands in the same relation to the thermionic emission of Chaps. III, IV and VI as the selective photoelectric emission of Chaps. IX and XIII to the normal photoelectric emission of Chaps. V and VI. In the case of the normal photoelectric emission we were also concerned with the emission of conduction electrons, and the influence of the adsorbed atoms consisted in the first instance in a change of the work function, thus in a shift of the photoelectric threshold, while in the case of the selective photoelectric emission we were concerned with a photoionization of adsorbed atoms whereby the electrons emitted were the valence electrons of the adsorbed atoms.

As we have already seen in § 79 the number of atoms which will lose their electrons by thermal ionization ( $n$ ) depends upon the total number of atoms adsorbed ( $n_0$ ) and upon the amount of energy ( $\Delta Q$ ) which must be given to an atom in order that it may emit its electron:

$$n_e = CC' n_0 e^{-\frac{\Delta Q}{kT}}.$$

If we are to have an electron emission here with a constant current of electrons, then the electrons emitted must be supplemented, just as was the case with the selective photoelectric effect. This supplementation through the dielectric intermediate layer here also helps to determine the size of the electron current. Upon this depends the frequency with which an adsorbed atom is placed in a condition to carry out the thermal ionization process. When, further, instead of the amount of energy  $\Delta Q$  we set

$$\Delta Q = \epsilon \phi_i,$$

where we may call  $\phi_i$  the work function in this case, we obtain the following formula for this thermionic emission:

$$i = A_i e^{-\frac{\epsilon \phi_i}{kT}},$$

where the constant  $A_i$  is proportional to the number of adsorbed atoms per cm.<sup>2</sup> ( $i$  is expressed in amp./cm.<sup>2</sup>), and further depends upon the number of times per second that an emitted electron can be supplemented or upon the number of

times per second that an adsorbed atom is able to emit its electron. We may on this basis expect that with the same dielectric and the same sort of adsorbed atoms the constant  $A_i$  will have very different values, dependent as it is upon the portion of the surface covered with adsorbed atoms, upon the roughness of the surface (the emission  $i$  is measured per cm.<sup>2</sup> of apparent surface), and especially upon the conduction of electrons through the lattice (thus also upon the occupation of the lattice by internally adsorbed atoms—see §§ 80, 81 and 90). On the other hand the “work function”  $\phi_i$  will not depend here in the first place upon the number of adsorbed atoms, any more than was the case with the photoelectric threshold of the selective photoelectric effect with those cathodes where atoms are adsorbed upon the surface of a dielectric (Chap. ix). In that case we saw that the position of the photoelectric threshold was entirely determined by the atoms which were bound at the most active spots. Just as in the photoelectric emission of this kind of cathode  $\phi_i$  is also given by those atoms which emit their electrons most easily and these atoms are already present at the most active spots when the smallest portion of the surface is occupied, so here also  $\phi_i$  will depend little or not at all upon the portion of the surface covered.  $\phi_i$  can of course take on other values if the “activity” of the active spots is changed, as we saw in Chap. XIII for the photoelectric threshold, or if the portion of the surface covered with adsorbed atoms becomes so great that regions are formed where conduction electrons may be considered to exist, in which case also the photoelectric threshold changes (usually withdraws to shorter wave-lengths, see § 65).

A photoelectric emission of the valence electrons of the adsorbed atoms themselves may also be observed when the atoms are adsorbed upon a metal surface (§ 70); in this case, however, the photoelectric threshold is still determined by the normal photoelectric effect, and one only observes the selective photoelectric effect at shorter wave-lengths, i.e. at higher energy values. We shall not, therefore, observe much of a thermionic emission of valence electrons of atoms adsorbed upon a metal surface, since the emission of conduction electrons

is always easier in such a case. The thermionic emission of valence electrons by thermal ionization will therefore be limited to those cases in which atoms of electropositive elements are adsorbed on surfaces of dielectrics.

In the descriptions of the emission of the cathodes which will be discussed in the following sections of this chapter, up to now use has been made, either without theoretical basis, or on the basis of an assumed mechanism in which conduction electrons were emitted, of the formulae for the electron emission of metal surfaces, namely (§ 2):

$$i = aT^{\frac{1}{2}}e^{-\frac{\epsilon\phi}{kT}},$$

or

$$i = AT^2e^{-\frac{\epsilon\phi_0}{kT}}.$$

This has little influence upon the value of  $\phi$  found, while we shall in the following sections where necessary recalculate the values of the other constants according to those of the above-mentioned formula

$$i = A_i e^{-\frac{\epsilon\phi_i}{kT}}.$$

### § 99. Thermionic emission of various caesium cathodes.

The [Ag]-Cs<sub>2</sub>O-Cs cathodes of § 68 and the [Ag]-Cs<sub>2</sub>O, Ag-Cs and [Ag]-Cs<sub>2</sub>O, Cs, Ag-Cs cathodes of §§ 94 and 95 are good examples of thermionic emitters which already give a high thermionic emission at very low temperatures (< 200° C.). Koller\* discovered that cathodes consisting of caesium on caesium oxide on silver give high values of thermionic emission at very low temperatures. The emission could be measured between 373 and 443° K., and could be represented by the formula

$$i = AT^2e^{-\frac{b}{T}},$$

where  $A = 9.8 \times 10^{-2}$  amp./cm.<sup>2</sup> and  $b = 8700^\circ$  ( $\phi_0 = 0.75$  volt). Recalculated for the formula

$$i = A_i e^{-\frac{\epsilon\phi_i}{kT}},$$

we obtain the values

$$A_i = \sim 1.1 \times 10^5 \text{ amp./cm.}^2 \text{ and } \phi_i = 0.82 \text{ volt.}$$

This value for  $\phi_i$  is very low when we consider that the photo-

\* L. R. Koller, *Phys. Rev.* **33**, 1082 (1929).

electric threshold of these cathodes in the most favourable case lies at  $1200\text{ m}\mu$ , and thus corresponds to a work function of more than 1 volt. Consideration of Fig. 107 in § 79 shows, however, that the energy connected with the thermal ionization of these adsorbed atoms does not have to be the same as the energy which corresponds to the photoionization. Since the Franck-Condon principle (§ 54) holds for the photoionization, we usually have to add a rather large amount of potential energy of the ion formed with respect to the adsorbing surface. In general, therefore, in these ionization processes the thermal ionization (difference in level between  $b$  and  $s$ ) will cost less energy than the photoionization (difference in level between  $b$  and  $g$ ), in other words, the thermionic work function will be less than the value of  $\phi$  corresponding to the photoelectric threshold.\*

Campbell† has investigated the thermionic emission of several  $[\text{Ag}]\text{-Cs}_2\text{O}$ ,  $\text{Cs}$ ,  $\text{Ag-Cs}$  cathodes at temperatures below  $200^\circ\text{C}$ . Quite in agreement with what we expected in § 98, he found that with various cathodes the values of  $A$  in the emission formula (thus also of  $A_i$ ) can differ very much, while the values for  $\phi_0$  (also therefore of  $\phi_i$ ) are practically the same. From his curves it can be seen that the values for  $A_i$  actually vary in a ratio of 1 to 200, while for  $\phi_0$  values of about 0.6 volt

are found. With reference to the formula  $i = A_i e^{-\frac{e\phi_i}{kT}}$  the values of  $\phi_i$  are somewhat greater (about 0.7 volt). It is nevertheless very striking how much smaller these values are than the values which correspond to the photoelectric threshold and which are given by Campbell at  $1300\text{ m}\mu$  at their maximum (0.95 volt).

During the preparation of the cathodes there is a parallelism between the course of the thermionic and that of the photoelectric emission; it is, however, striking that with various cathodes, those which give a high photoelectric emission have a low thermionic emission and *vice versa*.

\* J. H. de Boer, *Chem. Weekblad*, **29**, 34 (1932); J. H. de Boer and M. C. Teves, *Z. Phys.* **83**, 521 (1933).

† N. R. Campbell, *Phil. Mag.* **12**, 173 (1931).

The parallelism between thermionic emission and photoelectric emission during the preparation of the cathodes holds for the case where one starts with a cathode free of caesium upon which one slowly deposits caesium as Campbell does, as well as for the case where one begins with an excess of caesium, which is driven off by careful heating.\* In Fig. 143 can be seen the progress of both emissions for a  $[\text{Ag}]\text{-Cs}_2\text{O,Cs,Ag-Cs}$  cathode, after caesium atoms are adsorbed in the intermediate layer by heating in caesium vapour, as a function of the time of driving off the excess caesium. It can be seen that the emissions pass through a maximum at the same time, in other words, that the most favourable state of distribution of the caesium for the photoelectric emission is also the most favourable for the thermionic emission. It is remarkable that the thermionic emission is very low as long as small two-dimensional regions of cohering caesium atoms within which one may speak of conduction electrons are present on the surface. Only when we are concerned with individually adsorbed atoms (cf. also the absorption of light in § 62) does not only the photoelectric emission but especially also the thermionic emission assume large values, which again decrease when too many of the adsorbed atoms are removed from the surface by continued evaporation.

It must still be mentioned that the building in of caesium atoms not only increases the photoelectric emission but especially also the thermionic emission (cf. § 95).

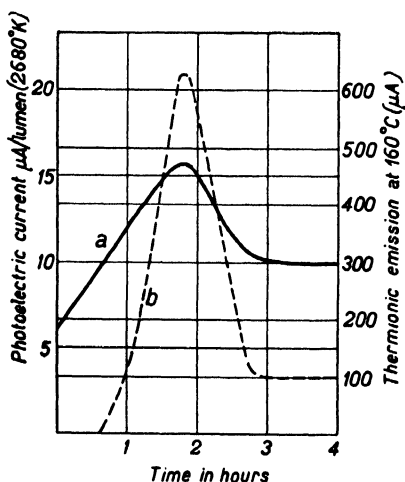


Fig. 143. Photoelectric (a) and thermionic (b) emission of a  $[\text{Ag}]\text{-Cs}_2\text{O,Cs,Ag-Cs}$  cathode as a function of the time of heating in order to vaporize the excess Cs.

\* J. H. de Boer and M. C. Teves, *Z. Phys.* **83**, 521 (1933).

### § 100. Oxide-coated cathodes; their preparation.

From a technical point of view the oxide cathodes (i.e. cathodes on which "activated" oxides of one or more of the alkaline earths, barium, strontium or calcium, deposited on a metal surface form the electron-emitting layers), are the most important ones. An important and detailed literature on this subject has appeared in the course of several years, including several very good survey articles.\* This is not the proper place to treat this subject in very great detail. We shall again only discuss these cathodes in as far as their properties are connected with the phenomena treated in this book.

Wehnelt† in 1904 had already discovered the strong emission of electrons by the oxides of the alkaline earths, barium, strontium and calcium, which is the reason why the oxide cathodes are sometimes called "Wehnelt cathodes". During the earlier years it was supposed that a chemical reaction was the cause of the strong electron emission, for example that barium and oxygen were formed from barium oxide, which upon their recombining to form barium oxide again would emit electrons.‡ Later it became apparent that we were dealing here with a thermal electron emission. We shall see below that this emission is connected with the presence of adsorbed alkaline earth metal, thus of adsorbed barium for example.

Oxide cathodes can be prepared by very different methods. Filaments or plates of very different metals are used as core (platinum, platinum-iridium, tungsten, nickel or nickel alloys). The oxide is practically never deposited as such, but a chemical compound is usually deposited from which the oxide results by heating, for example nitrate, hydroxide or carbonate. After deposition the compound is often sintered in air or in an

\* Cf. W. Schottky and H. Rothe, *Handbuch der Experimentalphysik*, 13, 2, pp. 215–31, Leipzig (1928); H. Simon, *Handbuch der Experimentalphysik*, 13, 2, pp. 305–14, Leipzig (1928); S. Dushman, *Rev. Mod. Phys.* 2, 418–44 (1930); A. Gehrts, *Naturwissenschaften*, 20, 732–9 (1932); A. L. Reimann, *Thermionic Emission*, pp. 188–232 (1934).

† A. Wehnelt, *Ann Phys.*, Lpz., 14, 425 (1904).

‡ K. Fredenhagen, *Phys. Z.* 15, 19 (1914); A. Gehrts, *Ber. dtsch. phys. Ges.* 15, 1047 (1913).



atmosphere of some other gas (often carbon dioxide when a carbonate is used). If the heating is carried out in air the chemical compound used can be decomposed immediately to give the oxide, while at the same time compounds are often formed at the border between oxide coating and core metal\* (platينات, nickelites, tungstates) which may again be partially decomposed later in the preparation and activation (§ 102) of the cathodes, and which give a grey to black, sometimes brownish intermediate layer between metal and oxide coating. Becker† calls such cathodes “combined” cathodes in contrast to the “uncombined” cathodes, where no chemical reaction takes place between core metal and coating during the preparation of the cathode and before the activation, and where the oxide coating has retained its whiteness up to the metal itself. Such uncombined cathodes can best be prepared when the chemical compounds used are decomposed to oxides in a vacuum.

Other methods of preparation of the oxide layers consist first of depositing the alkaline earth metal, barium for example, and then of oxidizing it, or just the reverse, of evaporating barium upon an easily reducible metal oxide layer. According to this last method, which is due to G. Hertz, the core metal (a platinum-rhodium filament or a tungsten filament) is first copper plated, the copper is oxidized, and barium is then distilled upon it. The barium reacts under application of heat with the copper oxide to give barium oxide and copper, which latter evaporates away. Most of the excess of barium also evaporates, to leave a definite number of adsorbed atoms, which, as we shall see in the following sections, determine the activity of the cathode.

In the preparation of technical oxide cathodes a mixture of barium oxide and strontium oxide is usually used (partly for mechanical reasons, the mixture adheres better). We shall return in § 106 to several unusual properties which distinguish these mixtures from pure oxides. Burgers‡ and Benjamin and

\* Cf. H. D. Arnold, *Phys. Rev.* **16**, 70 (1920).

† J. A. Becker, *Phys. Rev.* **34**, 1323 (1929).

‡ W. G. Burgers, *Z. Phys.* **80**, 352 (1933).

Rooksby\* showed that in many cases of the formation of the oxides from a mixture of the carbonates, layers consisting of mixed crystals of barium oxide and strontium oxide were obtained.

**§ 101. The presence of barium in BaO cathodes with high emission.**

As was stated in the previous section, the activity of the oxide cathodes which are good emitters is connected with the presence of adsorbed barium. Koller† in 1925 noticed the fact that oxide-coated filaments lose their efficiency, when they are heated to temperatures above  $1600^{\circ}\text{K}$ .; heating for from 1 to 5 minutes de-activates the filament. This decrease of the activity is not to be ascribed to the evaporation of the barium oxide; it can be directly observed that sufficient barium oxide is still present. From the measurements of the rate of evaporation of barium oxide by Claassen and Veenemans‡ it follows that in 5 minutes at  $1600^{\circ}\text{K}$ . with the usual thickness of the oxide coating ( $\sim 10^5$  molecular layers) only about 1/10 can be evaporated. By heating at a lower temperature ( $900^{\circ}\text{K}$ .) Koller could restore the activity. An impurity must thus have been removed by evaporation, which impurity is responsible for the electron emission, and which according to Koller is barium. In agreement with this is the fact that the activity of the oxide cathode is also destroyed by a short contact with oxygen (at a pressure  $> 10^{-3}$  mm.  $\text{O}_2$ ) or water vapour, while gases like argon or  $\text{CO}_2$ , which do not react with barium, do not poison the emissivity.

Other investigators have repeatedly confirmed these results of Koller and have also come to the conclusion that barium is essential for good emission.§ Becker|| could demonstrate directly that at  $1250^{\circ}\text{K}$ . metallic barium evaporates from a

\* M. Benjamin and H. P. Rooksby, *Phil. Mag.* **15**, 810 (1933); **16**, 519 (1933).

† L. R. Koller, *Phys. Rev.* **25**, 671 (1925).

‡ A. Claassen and C. F. Veenemans, *Z. Phys.* **80**, 342 (1933).

§ M. S. Glass, *Phys. Rev.* **28**, 521 (1926); H. Rothe, *Z. Phys.* **36**, 737 (1926); W. Espe, *Wiss. Ver. Siemens-Konz.* **5**, 3es Heft, 29 (1927); F. Detels, *Jb. drahtl. Telegr.* **30**, 10, 52 (1927).

|| J. A. Becker, *Phys. Rev.* **34**, 1323 (1929).

well-activated oxide cathode, by capturing the barium on a tungsten filament which was thereby converted into a [W]-Ba cathode (§ 32). On the other hand Becker could also bring a non-activated oxide cathode into a state where it was a good emitter by distilling barium upon it from an external source. It is remarkable that with increasing amount of barium the electron emission (measured at a constant temperature (600° K.) and a constant tension (70 volts) between cathode and anode) first rises and then after passing through a maximum again falls to a constant value, so that here again as with the cathodes where caesium is adsorbed on caesium oxide (§ 99) we come to the conclusion that there is a maximum in the sensitivity when there is a definite number of atoms adsorbed. Similar results were obtained by Becker when he caused the formation of barium atoms in the surface of the oxide by sending electrons into the oxide from an outside source and thereby electrolyzing the oxide. In this method also a maximum of the emission was passed when too great an amount of adsorbed barium had been formed. If there is too much barium adsorbed upon the oxide, the emission may again be made to rise by carefully evaporating the excess.

The barium atoms which evaporate from a glowing oxide cathode can also be demonstrated spectroscopically.\* The amount of barium atoms adsorbed upon the barium oxide can be determined quantitatively by measuring the amount of hydrogen resulting from the reaction with water vapour† or by measuring the amount of oxygen which can be taken up in the oxidation of these barium atoms to barium oxide. Both methods have been applied by Clausing‡ with the common result that with the cathodes used by him about  $\frac{1}{4}$  per cent. of the total number of barium oxide molecules were reduced to barium atoms. If there are 10 milligrams of the oxide coating per cm.<sup>2</sup> of outside surface ( $4 \times 10^{19}$  molecules of BaO per cm.<sup>2</sup>) there are  $10^{17}$  free barium atoms per cm.<sup>2</sup> of the cathode surface,

\* A. Gehrts, *Z. techn. Phys.* **11**, 246 (1930); *Naturwissenschaften*, **20**, 732 (1932).

† T. P. Berdennikowa, *Phys. Z. Sowjet.* **2**, 77 (1932).

‡ P. Clausing (unpublished).

at least if these barium atoms are all situated on the cathode. If these latter should be situated upon an area of the outside surface (considered smooth) of  $1 \text{ cm.}^2$  they would give a continuous layer of barium of 200 atoms thickness. The adsorbed layer of barium atoms is, however, at the most one atom thick, while it is not improbable that the occupation of the surface by barium atoms is much smaller. Probably here also, as in the adsorption of caesium atoms on fluoride layers (§§ 62 and 65) or of caesium atoms on caesium oxide layers (§ 68), the portion of the surface covered which is most favourable for emission (cf. also § 99) is distinguished by the complete occupation of all the available active spots on the surface, without the adsorbed atoms forming small continuous regions in which it would be possible to speak of conduction electrons. Measurements relating to the adsorption of caesium on calcium fluoride\* seem to indicate that the most favourable state is reached when the surface is about one-third covered. If we assume a similar result for the adsorption of barium on barium oxide, it would mean that the actual surface of the barium oxide as used by Clausen in his experiments was about  $600 \text{ cm.}^2$ , thus 600 times as great as the outside surface when it was assumed to be smooth. The layers used are actually very porous and possess a very large true surface. On the other hand, however, it is also possible that barium has penetrated here into the lattices of the various grains of barium oxide and is there adsorbed upon places of disturbance or internal surfaces. Phenomena relating to the supplementation of electrons which we shall examine more carefully in § 104 indicate that a building in of barium atoms into the barium oxide is in fact probable. Future experiments will have to show among other things how great is the actual surface which can be reached from the outside of the barium oxide on the oxide-coated filaments, and how many barium atoms are adsorbed within the lattice of barium oxide.

It must be noted that, in the building in of alkali metal atoms into the lattices of the alkali halides whereby the

\* J. H. de Boer and C. J. Dippel, will be published shortly in *Rec. Trav. chim. Pays-Bas*.

lattices become electronic conductors, a smaller percentage of alkali metal atoms is usually used. It was mentioned in § 80 that in Stasiw's experiments there is one alkali metal atom per  $10^5$  molecules of alkali halide.\* In these experiments, however, only built-in atoms are present and no atoms are adsorbed on the outside surface. In technical photocells as described in §§ 94 and 95 there are often 5 to 20 or more caesium atoms per 100 molecules of caesium oxide adsorbed upon internal and external surfaces together.

### § 102. The process of "activating" or "forming".

The barium adsorbed upon the surface and in the lattice of the barium oxide must either be introduced from an outside source, or it must be formed from the barium oxide itself. In the method mentioned in § 100, where the oxide-coated filament was formed by evaporating barium upon a copper oxide layer, and allowing it to react, the excess barium is evaporated away to give the desired amount of adsorbed barium, and further activation of the cathode is unnecessary. In the previous section we saw that Becker distilled barium on an inactive barium oxide cathode and obtained in this manner an active layer. In almost all the other methods for the activation of oxide cathodes the desired amount of barium is formed from the barium oxide, which reaction can be brought about by means of some reducing agent or by electrolysis. It has often been thought that the barium can be formed from barium oxide simply by heating, i.e. by thermal dissociation.† On the basis of the extraordinarily low dissociation pressure of barium oxide this view must, however, be dismissed. Dushman and Villars‡ give as oxygen equilibrium pressure over barium oxide at  $1000^\circ$  K. a value of  $< 10^{-40}$  atmosphere, while Becker§ gives a pressure of  $10^{-35}$  mm. Hg or lower. Even in the best vacuum which can practically be reached ( $\sim 10^{-10}$

\* According to a recent investigation of E. Mollwo, *Nachr. Ges. Wiss. Göttingen*, Neue Folge, 1, 79 (1934), the concentration of Ca atoms in  $\text{CaF}_2$  may be much higher than the concentration of alkali atoms in alkali halide crystals and may have values of several per cent.

† A. Gehrts, *Z. techn. Phys.* 11, 246 (1930).

‡ S. Dushman and D. S. Villars, *Rev. Mod. Phys.* 2, 433 (1930).

§ J. A. Becker, *Trans. Electrochem. Soc.* 59, 207 (1931).

mm. Hg) it is impossible to dissociate barium oxide thermally. When every reducing agent in the layer or in the surroundings (core filament, gas) is entirely excluded, it is impossible to activate unactivated oxide-coated filaments by heating alone.\* Neither could Berdennikowa prove the formation of barium under similar conditions by simple heating to 1200° C.;† barium was only formed by electrolytic decomposition of the barium oxide.

By reduction, however, the necessary quantity of barium can be formed. In many cases the presence of some organic binding material in the original layer is enough. When in the "uncombined" cathodes (§ 100) the chemical compound used is decomposed by heating in a vacuum to give the oxide, enough carbon or reducing carbon compounds are usually formed from the binding material to reduce a portion of the barium oxide. Clausing,‡ in the experiment mentioned in §101, found that by this reduction already as much barium can be formed as is necessary for the good emission of the cathode; further activation of these cathodes is then unnecessary. The reduction can also be brought about by the reaction of the core metal or of components of the core metal with the oxide coating. Lowry§ investigated simultaneously an alloy of platinum with 10 per cent. iridium and an alloy of nickel, cobalt, iron and titanium called "Konel", as core filaments for the oxide coating. In contrast to the cathodes with the platinum-iridium core, the oxide coatings on Konel as core were activated by heating alone. Probably when Konel is used a portion of the barium oxide is reduced by a reaction of one or more of the components of the core metal (Fe, Ti). Beese|| uses an alloy of nickel with 0.15 per cent. barium as core metal and attains a higher emission than by the use of pure nickel alone. With nickel alone as core metal a reduction of barium oxide at sufficiently high temperature is not impossible.

\* W. Meyer and A. Schmidt, *Z. techn. Phys.* **13**, 137 (1932).

† T. P. Berdennikowa, *Phys. Z. Sowjet.* **2**, 77 (1932).

‡ P. Clausing (unpublished).

§ E. F. Lowry, *Phys. Rev.* **35**, 1367 (1930).

|| N. C. Beese, *Phys. Rev.* **36**, 1309 (1930).

If, however, the possibility of the reduction of the barium oxide by some reducing agent is excluded, the cathode must be activated by electrolysis. In the case of the "combined" cathode this is in general the case, since during the heating in air reducing agents present in the coating and also in the intermediate layer between oxide coating and core metal are oxidized and thus rendered inactive. Unactivated oxide coatings conduct electrolytically at sufficiently high temperatures.\* The electrolytic conductivity can be represented by the formula

$$\kappa = Ce^{-\frac{Q}{RT}} \quad (\text{cf. } \S 81),$$

or by a sum of two such powers of  $e$ , and thus increases rapidly with the temperature. Since in this electrolysis electrons are drawn from the coated filament, barium is deposited on the core-oxide interface and oxygen on the outer surface. The barium atoms diffuse—probably along the crystal boundaries (cf. § 34)—through the oxide coating to the outside surface and are there adsorbed. During the electrolysis the portion of the surface covered with barium atoms increases simultaneously with the external emission of electrons, in other words the filament is activated. As we shall see in § 104, some investigators assume that in the activated state the conduction through the layer is also entirely of electrolytic nature. It is, however, much more probable, as is assumed by most investigators, that, while to be sure the flow of current through the oxide coating is of electrolytic nature during the electrolytic activation, according as the cathode becomes more activated the conduction becomes more electronic, so that in the completely activated cathode the current is conducted chiefly by electrons.†

In the electrolytic decomposition during the activation process oxygen and barium are formed. The development of gas (oxygen) during the activation has repeatedly been observed,‡

\* Cf. W. Meyer and A. Schmidt, *Z. techn. Phys.* **13**, 137 (1932).

† Cf. J. A. Becker, *Phys. Rev.* **34**, 1323 (1929); W. Meyer and A. Schmidt, *Z. techn. Phys.* **13**, 137 (1932); A. Gehrts, *Naturwissenschaften*, **20**, 734, 736 (1932).

‡ F. Horton, *Phil. Mag.* **11**, 505 (1906); H. A. Barton, *Phys. Rev.* **26**, 360 (1925); H. Rothe, *Z. Phys.* **36**, 737 (1926).

while Detels\* identified this gas as oxygen. When large currents are drawn from barium oxide and strontium oxide coated filaments, barium and strontium are present in the core,† which is not true if the filaments are merely heated to a high temperature without a current being allowed to flow through the oxide coating. When platinum is used as core metal such a formation of an alloy can easily take place.‡ As was mentioned above the activation occurs in this electrolysis by the diffusion of barium atoms to the outside and the adsorption of the barium upon the outer surface and also in the oxide. Another method of electrolytic activation was mentioned in § 101, viz. by sending electrons into a coated filament from another source.§ As a further method of activation may be mentioned bombardment of the cathode with positive gas ions, for example positive ions formed in  $\text{CO}_2$ .||

### § 103. The mechanism of the emission of oxide-coated filaments.

It is now generally agreed that the good emission of oxide cathodes is due to the presence of free alkaline earth metal. One finds in the literature, however, rather varied views as to the manner in which the emission due to the alkaline earth metal is brought about or increased.

The first problem to be solved is whether the source of the emission is to be sought on the surface of the core metal or on the surface of the oxide coating. Lowry¶ supposes that the emission comes from a layer of metallic barium occluded on the surface of the core metal or alloyed with it. He bases his opinion upon his experiment mentioned in § 102 with Konel as core metal and also upon the circumstance that in the electrolytic activation the barium comes directly to the core. The electrons emitted must diffuse through the pores in the

\* F. Detels, *Jb. drahtl. Telegr.* **30**, 10, 52 (1927).

† J. H. Harris, mentioned by J. A. Becker, *Phys. Rev.* **34**, 1327 (1929).

‡ Cf. for example T. P. Berdennikowa, *Phys. Z. Sowjet.* **2**, 77 (1932).

§ J. A. Becker, *Phys. Rev.* **34**, 1323 (1929).

|| V. C. Macnabb, *J. Opt. Soc. Amer.* **19**, 33 (1929); cf. also L. R. Koller, *Phys. Rev.* **25**, 671 (1925).

¶ E. F. Lowry, *Phys. Rev.* **35**, 1367 (1930).



oxide coating. He is able to explain various properties of the oxide cathode emitters by means of this diffusion of electrons.

Reimann and Murgoci\* also ascribe a primary part to the emission of electrons from the core metal. According to their view the electrons are, to be sure, emitted from the outside surface, and they picture this emission in a way which corresponds with the conception developed in § 98 and elsewhere (see further in this section), but since the coating is probably in very imperfect contact with the core metal, the electrons of the core metal must be emitted thermionically and recaptured by the coating, which re-emits the electrons. It is possible that the crystals of the coating are even in poor contact with one another and that therefore each crystal must be supposed to collect electrons on its inner surface and re-emit them from its outer. We shall return to this conception in more detail in the following section, and make only this remark, that the thermionic emission of the cathode as a whole in the view developed by Reimann and Murgoci must be limited by the coating or by the core metal. According to Reimann and Murgoci and also to Reimann and Treloar† it appears that, at least in certain cases, it is the core metal, and not the coating, by which the emission is limited. In principle they regard the oxide cathode thus as a metal cathode upon whose surface barium atoms and possibly oxygen atoms (or both as ions) are adsorbed, thus as the [W]-Ba cathodes of § 32 or the [W]-O,Ba cathodes of § 50. Reimann has recently stated that the emission is not limited by the core.‡

Not only through the experiments of Becker which we discussed in the foregoing sections (activation by distilling barium on the oxide or by sending electrons into it from another source), but also by various experiments by Becker and Sears§ has it been shown that the source of emission is not the surface of the core metal, but that the electrons come primarily from the outer surface of the oxide coating. The oxide coating of

\* A. L. Reimann and R. Murgoci, *Phil. Mag.* **9**, 440 (1930).

† A. L. Reimann and L. R. G. Treloar, *Phil. Mag.* **12**, 1073 (1931).

‡ A. L. Reimann, *Thermionic Emission*, p. 212 (1934).

§ J. A. Becker and R. W. Sears, *Phys. Rev.* **38**, 2193 (1931).

some filaments can easily be shaken off—which agrees with the assumption of poor contact of Reimann and Murgoci—the remaining core metal then, however, shows no high emission. Still more convincing are the experiments in which the co-operating interface between core metal and oxide coating may be varied in size without changing the outer surface of the oxide coating. It appeared that this had no influence upon the emission, which would have been the case if the surface of the core metal were primarily responsible for the emission. Becker and Sears therefore conclude that the electrons come from the outer surface of the oxide coating and that the part played by the core metal is an indirect one, in as much as under the influence of reduction the concentration of barium adsorbed on the surface of the oxide or dispersed through the oxide may increase (cf. § 102), or the composition or physical structure of the oxide may change.

It is also assumed by various other investigators that the electrons come primarily from barium adsorbed on the outer surface. Thus Espe\* assumes that the metallic barium forms small regions on the oxide surface, small islands, which emit their conduction electrons in a normal way. It is hereby actually assumed that the work function of such an oxide cathode is equal to the work function of the alkaline earth metal under consideration, an assumption which is also made by Gehrts.† For this it would actually be necessary for the barium to be distributed upon the oxide surface in such a way that relatively large continuous regions of barium atoms occurred whose physical state already corresponded in various respects to some extent with that of ordinary metallic barium.

In §§ 62 and 65 in the study of the adsorption of caesium atoms on fluoride layers we saw that when large fractions of the surface are covered such continuous regions of caesium do exist, which can be compared with normal caesium as shown by the absorption spectrum.‡ At the same time, however, we saw that the maximum photoelectric emission is reached when

\* W. Espe, *Wiss. Ver. Siemens-Konz.* 5, 3es Heft, 29 (1927).

† A. Gehrts, *Naturwissenschaften*, 20, 732 (1932).

‡ J. H. de Boer, J. F. H. Custers and C. J. Dippel, *Physica*, 1, 935 (1934).

small fractions of the surface are covered and there is still no question of continuous regions of caesium, but rather of individually situated caesium atoms, the surface being practically colourless.\* We saw further in § 99 that with such cathodes in which caesium atoms are adsorbed on caesium oxide, at a definite occupation of the surface by caesium atoms, the photoelectric and the thermionic emission both exhibit an optimum. At this optimum the active spots of the surface are probably just completely occupied by atoms, which are adsorbed chiefly by means of electrostatic forces (see §§ 16, 61, 62). If fewer caesium atoms are present then the photoelectric as well as the thermionic emission is smaller, simply because of the fact that there are fewer emission centres. If there are more caesium atoms present, these caesium atoms are bound by van der Waals' forces to the surface next to those already present and to each other (§ 16), giving rise to regions where conduction electrons may be present, and may be emitted. Both emissions now also become smaller since we pass over to a quite different mechanism of emission, whereby the work function is increased, and also—this holds for the photoelectric emission—the yield of electrons per quantum of light absorbed is very low.

From the experiments of Becker† we know that also in the case of the oxide-coated filaments the emission as a function of the quantity of barium exhibits a maximum when a definite fraction of the surface is covered (§ 101). It is therefore not impossible that with these cathodes also barium atoms, and not continuous regions of barium, are the source of the emission at the state of optimum emission. The very existence of this optimum in the emission at a definite concentration of adsorbed barium caused Becker and Sears‡ to decide that although the electrons come from the outer surface of the oxide, the process is analogous to that with double layers on metals, namely that conduction electrons are emitted from the oxide whose work function is very much lowered by the presence of adsorbed

\* J. H. de Boer and M. C. Teves, *Z. Phys.* **65**, 489 (1930).

† J. A. Becker, *Phys. Rev.* **34**, 1323 (1929).

‡ J. A. Becker and R. W. Sears, *Phys. Rev.* **38**, 2209, 2212 (1931).

barium. They came to this conclusion mainly because the existence of the above-mentioned optimum could not otherwise be explained. On the basis of the above, however, we see that this optimum can be understood in the light of our present knowledge.

If in these oxide cathodes also we consider the primary cause of the emission to be a thermal ionization of adsorbed atoms, the cathodes are similar in principle to the caesium cathodes treated in § 99. We must, as in that case, also expect that cathodes which vary in amount of barium adsorbed on the surface and in the oxide will exhibit practically the same work function  $\phi_i$  (cf. § 98), but that the constant  $A_i$  in the emission formula will vary very much. It must be noted that also in the emission of electrons from continuous regions of barium a variation in the value of  $A$  and a constancy in the value of  $\phi_0$  is to be expected. In a detailed examination Espe\* found this expectation confirmed in reality. Not only with his calcium oxide, but also strontium oxide and barium oxide cathodes the

values of  $A$  in the formula  $i = AT^2 e^{-\frac{\epsilon\phi_0}{kT}}$  varied from  $0.2 \times 10^{-3}$  to  $20 \times 10^{-3}$  amp./cm.<sup>2</sup> and the  $\phi_0$  values were quite constant (for CaO,  $1.77 \pm 0.03$  volts; for SrO,  $1.27 \pm 0.025$  volts; for

BaO,  $0.99 \pm 0.03$  volts). Recalculated for the formula  $i = A_i e^{-\frac{\epsilon\phi_i}{kT}}$  Espe's values become, for BaO,  $\phi_i = 1.15$  volts and  $A_i$  varying between  $1.25 \times 10^3$  and  $1.25 \times 10^5$  amp./cm.<sup>2</sup> (cf. the values for the caesium cathodes in § 99). With other investigators also the values of  $A_i$  vary about 1 to 100, while the value of  $\phi_i$  is fairly constant.† This large variation is due, besides to differences in fraction of the surface covered with barium, also to variations in the supplementation of electrons, since  $A_i$  is of course dependent on the number of times per second that a surface atom can be ionized thermally (§ 98). With Becker and Sears‡ we also agree that the barium dispersed through the oxide increases the  $A$  ( $A_i$ ) in the emission equation.

\* W. Espe, *Wiss. Ver. Siemens-Konz.* 5, 3es Heft, 29, 46 (1927).

† Cf. H. Kniepkamp and C. Nebel, *Wiss. Ver. Siemens-Konz.* 11, 2es Heft, 75 (1932).

‡ J. A. Becker and R. W. Sears, *Phys. Rev.* 38, 2210 (1931).

If the oxide cathodes are allowed to emit electrons for very long times (hundreds to thousands of hours) the emissivity finally decreases. In agreement with the above Clausing\* found that the  $\phi_0$  also remains practically unchanged, the  $A$  value (or  $A_i$  value), however, decreases. Thus with the cathodes examined by him the value of  $A$  could fall to 1/100 of its original value while  $\phi_0$  only decreased for example from 1.20 to 1.15. Such measurements are reliable only when the state of the surface of the cathode does not change qualitatively, for example by the combining with oxygen or adsorption of oxygen. Variations in the quantity of barium are manifested in the change in  $A_i$ , which indicates that the barium atoms themselves are here the source of the emission and that they do not change the work function of the oxide as would a double layer. We shall return in § 105 to the variations in  $\phi_i$  by chemical changes on the surface.

#### § 104. The mechanism of the supplementation of electrons.

Just as important as the mechanism of the direct electron emission is the mechanism of the supplementation of electrons. The opinions about the conduction through the oxide layer of a well-activated oxide cathode vary as much as the views about the emission itself. There are proponents of a pure electrolytic conduction and proponents of an electronic conduction or of a mixed conduction.

In the picture proposed by Reimann and Murgoci† the electrolytic conduction plays a great part. When a barium atom on the surface of the oxide cathode has emitted its electron, the ion formed is, according to these authors, drawn to the inside as a positive ion. When this ion has arrived upon the inner surface through the oxide crystal, it is there neutralized by the capture of an electron which is emitted from an oxide crystal lying deeper within. The barium atom formed by neutralization now diffuses along the surface of its own crystal again to the outer surface, where it may again lose its electron, and so on. In each crystal of the oxide coating

\* P. Clausing (unpublished).

† A. L. Reimann and R. Murgoci, *Phil. Mag.* 9, 440 (1930).

(or in the coating as a whole) there is thus a circulation of barium: barium ions are displaced from the outside to the inside through the crystal, barium atoms from the inside to the outside along the crystal. In their conception the electrons are transported to the outer surface, at least in the case of one small crystal, by surface migration after having joined a barium ion to give a barium atom. Thus between the small crystals emission and capture of electrons takes place. The conduction through the lattice is, according to them, entirely of electrolytic nature, and barium ions are the moving bodies.

One of the best arguments for the electrolytic conduction was the dependence on temperature according to a power of  $e$ , such as is found in electrolytic conduction. Now we have previously seen (§§ 79, 80, 90) that the electronic conduction of semi-conductors and dielectrics also varies with the temperature according to a power of  $e$ . In spite of this Reimann and Treloar\* consider an electrolytic conduction the most probable not only for an unactivated cathode but also for an activated cathode.

Without doubt the conduction of an unactivated cathode during the process of activation is of electrolytic nature; barium and oxygen are hereby formed and one may demonstrate polarization phenomena. The conduction may according to Becker,† as well as Meyer and Schmidt,‡ be represented by a sum of two powers of  $e$ . After the formation of the cathode, however, according to Meyer and Schmidt, the conduction is entirely of electronic nature and can be represented by the formula

$$\kappa = 0.123e^{-\frac{3480}{T}}.$$

Meyer and Schmidt assume in this case the formation of a barium suboxide,  $\text{Ba}_x\text{O}$ , which would conduct electronically. Benjamin and Rooksby§ found by means of X-rays only the compound  $\text{BaO}$ . It must, however, be noted that a  $\text{BaO}$  lattice

\* A. L. Reimann and L. R. G. Treloar, *Phil. Mag.* **12**, 1073 (1931).

† J. A. Becker, *Trans. Electrochem. Soc.* **59**, 207 (1931).

‡ W. Meyer and A. Schmidt, *Z. techn. Phys.* **13**, 137 (1932).

§ M. Benjamin and H. P. Rooksby, *Phil. Mag.* **15**, 810 (1933).

in which barium atoms are dispersed could also be called a suboxide in the sense of Meyer and Schmidt.

During the activation the conduction through the oxide layer increases, and it increases entirely parallel to the increase of the electron emission, while both may be poisoned by the same agents.\* Albright† found a linear relation between the conductivity and the emission of electrons during the formation, and also assumed that both phenomena were due to barium. The fact that the conductivity increases with the increase in the amount of barium dispersed in the oxide is a strong argument for electronic conduction. The barium oxide, by the formation of internally adsorbed barium atoms, becomes an electronic semi-conductor of the type which we met with in §§ 81 and 90. On the basis of the measurements known from the literature on the conductivity of such activated oxide layers Fowler and Wilson‡ also came to the conclusion that the whole current-voltage-temperature relationship can be explained on the supposition that the current is chiefly electronic.§ The electrolytic portion increases in importance relatively to the electronic part at low temperatures. Especially the well-known fact that on changing the anode potential the current only slowly reaches its equilibrium value|| can easily be explained on the basis of this view. A concentration gradient of  $Ba^{++}$  and  $O^{--}$  will be formed by the electrolytic portion of the currents; this gradient opposes the electrolytic as well as the electronic current in the oxide; it promotes, however, the transfer of electrons from metal to oxide and from oxide to metal (the measurements of the conductivity were naturally carried out between two metal contacts). This last effect may overcompensate the polarization in the lattice. When the tension is lowered the concentration of the ions will not immediately be established for the lower equilibrium value. Until this is done an electron current will

\* A. L. Reimann and R. Murgoci, *Phil. Mag.* **9**, 440 (1930).

† W. Albright, *Physica*, **11**, 146 (1931).

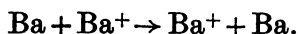
‡ R. H. Fowler and A. H. Wilson, *Proc. roy. Soc. A*, **137**, 503 (1932).

§ Cf. also A. L. Reimann, *Thermionic Emission*, pp. 212-27 (1934).

|| J. A. Becker, *Trans. Electrochem. Soc.* **59**, 207 (1931); A. L. Reimann and L. R. G. Treloar, *Phil. Mag.* **12**, 1073 (1931).

flow which is greater than the equilibrium value for the new voltage.

The conduction will thus be chiefly electronic, and the current will be carried by electrons which travel from barium atom to barium atom in the layer, each time transforming these atoms temporarily into ions. This conductivity may be represented in a manner analogous to that in § 81 by



This conception has an analogy with that of Reimann and Murgoci for the jump of the electrons from one crystal to another. The difference is that in our conception the electrons move through the lattice and in that of Reimann and Murgoci through the vacuum in order to pass from the one crystal to the other, while in the crystal a different (see above) mechanism provides the conduction. From the above-mentioned formula of Meyer and Schmidt for the conductivity through the activated layer it follows that an energy of 0.3 electron volt is necessary to break the electrons from the internally adsorbed atoms by thermal energy and to emit them into the lattice. Clausen\* found similar values for well-activated cathodes. It is important to mention that it follows from the measurements of Clausen that after prolonged emission from oxide cathodes, whereby, as we saw in the foregoing section, the  $A_i$  value in the formula for the emission decreases very much and the  $\phi_i$  remains practically constant, the work function for the internal emission (conduction) does not seem to change, and that at the same time the constant for the power of  $e$  in the conduction formula also remains unchanged. In a certain series of measurements for example, for the  $A$  and  $\phi_0$  values

of the emission formula,  $i = AT^2 e^{-\frac{\phi_0}{kT}}$ , the following values were found at the start,  $A = 0.96$ ,  $\phi_0 = 1.20$ , and after more than 1000 hours,  $A = 0.25$ ,  $\phi_0 = 1.15$ , while for the constants of

the formula for the conductivity  $\kappa = Ce^{-\frac{\psi}{kT}}$ , at the start  $C = 6.73 \times 10^{-3}$  and  $\psi = 0.273$ , and after more than 1000 hours  $C = 13.4 \times 10^{-3}$  and  $\psi = 0.271$ . From this behaviour one might

\* P. Clausen (unpublished).



conclude that it is only the portion of the outside surface covered with adsorbed atoms emitting electrons directly to the outside, which has decreased in the course of time.

Besides the electronic conduction which chiefly transports the current through the oxide layer, there is still as we saw above a small electrolytic conduction always present.\* Every emitting oxide cathode loses not only barium oxide but also barium atoms by evaporation, while under some circumstances oxygen is also liberated, which is either adsorbed at the surface (see also § 105) or is evaporated as such. The small electrolytic component of the conduction provides for a replacing of the barium atoms lost in this way.

In brief the whole conception comes down to this, that during the activation barium atoms are formed (oxygen also if the activation is electrolytic), which are adsorbed on the outer surface and also in the oxide lattice. The adsorbed atoms can lose their electrons by thermal ionization; the emitted electrons are replaced through the layer by being passed on from internally adsorbed atom to internally adsorbed atom. Finally electrons out of the core are supplied to the ionized, internally adsorbed atoms in the oxide due to the strong electric fields which these ions cause at the surface of the metal (§ 9). We may thus indicate such a cathode by the symbol [Me]-BaO,Ba-Ba.

### § 105. Changes in the state of the cathodes during emission.

In § 96 in the discussion of the supplementation of electrons in photocathodes with relatively thick intermediate layers we met several phenomena which indicated that the state of the cathode changes during the emission under certain circumstances. The fall in emission was there in part to be ascribed to the presence of positive caesium ions on the surface which remained temporarily unneutralized (electrons stuck in the layer by excitation), in part also the surface was impoverished because of the fact that the positive caesium ions were drawn to the inside (electrolytic cause of fatigue). The temporary non-neutralization of a number of positive ions on the surface

\* Cf. J. A. Becker, *Phys. Rev.* **34**, 1323 (1929).

results in a withdrawal of the photoelectric threshold (increase of  $\phi_i$ ); the impoverishment of the surface with respect to adsorbed atoms by electrolytic migration in the form of positive ions results in a decrease in the number of emission centres (decrease of  $A_i$ ).

In the thermionic emission because of the high temperature no influence of excitation can be expected. The electrolytic impoverishment, however, may still play a part. [Ag]-Cs<sub>2</sub>O, Ag-Cs and [Ag]-Cs<sub>2</sub>O, Cs, Ag-Cs cathodes actually show such a phenomenon.\* At a temperature of about 150°C., with a tension between anode and cathode of 250 volts, the emission decreases continually, while at 50 volts it again increases continually.

Such a phenomenon is also found with oxide-coated filaments; the emission there also decreases with the time, sometimes quite rapidly.† Gehrts‡ explains this decrease in the emission, in agreement with the above, as a temporary impoverishment of the surface with respect to barium. If after the decrease in emission the system is heated for a time with no current flowing, the original state with a high emission is recovered. Gehrts assumes that the  $\phi_0$  becomes larger during this decrease of the emission which is caused by the fall in the number of barium atoms on the surface. If actually merely a decrease in the number of barium atoms takes place, this increase of  $\phi_0$  is improbable and we should rather expect, on the basis of the material in §§ 98 and 103, that the  $A_i$  in the emission formula would decrease. Kniepkamp and Nebel§ have worked out an oscillograph method of rapidly measuring the constants of the emission equation. In this investigation it appeared that, during the first interval of time while the emission current is decreasing, the constant  $\phi_i$  remains constant and  $A_i$  decreases. Referred to the formula  $i = A_i e^{-\frac{\epsilon\phi_i}{kT}}$  the value

\* J. H. de Boer and M. C. Teves, *Z. Phys.* **83**, 531 (1933).

† Cf. C. Davisson and L. H. Germer, *Phys. Rev.* **24**, 666 (1924); H. Rothe, *Z. Phys.* **36**, 737 (1926); J. A. Becker, *Phys. Rev.* **34**, 1323 (1929).

‡ A. Gehrts, *Z. techn. Phys.* **11**, 246, 252 (1930).

§ H. Kniepkamp and C. Nebel, *Wiss. Ver. Siemens-Konz.* **11**, 2es Heft, 75 (1932).

of  $\phi_i$  remained constant at 1.22 volts, while  $A_i$  decreased from  $5.9 \times 10^5$  amp./cm.<sup>2</sup> to  $1.5 \times 10^5$  amp./cm.<sup>2</sup>

It appeared, however, in addition that with continued emission still another phenomenon makes its appearance, whereby the value for  $A_i$  again increases and that of  $\phi_i$  rises. This phenomenon is also electrolytic. Not only the barium ions but also the oxygen ions may move through the layer and arrive at the outer surface as oxygen ions, there to be finally neutralized and form a polarized layer. Kniepkamp and Nebel in agreement with Becker\* and others ascribe these further changes to the oxygen. As we saw in the previous section, Becker showed that with the removal of larger currents oxygen also evaporated from the surface. Due to the accumulation of oxygen on the surface  $\phi_0$  may rise to 1.7 when reference is made to the formula

$$i = AT^2 e^{-\frac{e\phi_0}{kT}} (\phi_i = 1.95 \text{ referred to the formula } i = A_i e^{-\frac{e\phi_i}{kT}}).$$

The fact that the constant  $A$  also increases was known by Kniepkamp and Nebel from a dependence of  $\phi_0$  on temperature, in the same way as was discussed in § 49.

During electrolytic activation such an oxygen covering is also present on the surface, and only evaporates away toward the end of the activation, or may perhaps be bound by barium diffusing to the outside. If the values of  $\phi_0$  ( $\phi_i$ ) are measured during the activation, it is found that they decrease.† Huxford‡ measured the change of the photoelectric threshold during the activation and found that in the last phase of the process it was shifted from about 6200 Å. to 9300 Å. (corresponding to values of  $\phi$  from 2.0 to 1.32 volts).

### § 106. Poisoning and recovering of cathodes.

As was mentioned in § 101 and elsewhere the activity of an oxide cathode may be destroyed by oxygen. This is a much more serious affair than the rise of  $\phi_i$  due to small amounts

\* J. A. Becker, *Trans. Electrochem. Soc.* **59**, 207 (1931); J. A. Becker and R. W. Sears, *Phys. Rev.* **38**, 2193 (1931).

† F. Detels, *Jb. drahtl. Telegr.* **30**, 10, 52 (1927).

‡ W. S. Huxford, *Phys. Rev.* **38**, 379 (1931).

of oxygen formed during the emission by electrolysis. Cold as well as hot oxide cathodes are completely de-activated by a sufficiently high pressure of oxygen ( $> 10^{-3}$  mm.),\* since all the barium atoms are oxidized. The barium atoms in the oxide are also oxidized either directly or later during the heating, so that not only the emission but also the conductivity of the layer is poisoned.† Poisoning is also evidenced after the admission of water vapour or after a discharge in carbon monoxide or in hydrogen.

After such a poisoning re-activation is possible. If, however, the cathode is repeatedly poisoned and re-activated, the re-

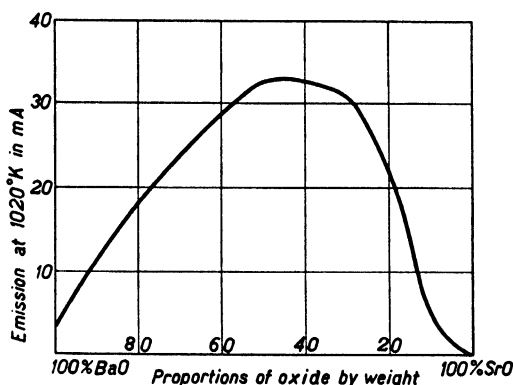


Fig. 144. Thermionic emission of oxide-coated filaments coated with mixed crystals of BaO and SrO, as a function of the composition of those mixed crystals. M. Benjamin and H. P. Rooksby, *Phil. Mag.* 15, 821 (1933).

activation becomes very difficult, at least when the cathode consists of a mixture of strontium and barium oxides. Thus Reimann and Murgoci state that complete recovery of the former condition by re-forming is possible only a few times in succession after poisonings by oxygen or by a discharge in carbon monoxide. They ascribe this to a growing together or a sintering together of the porous layer. Benjamin and Rooksby,‡ however, find that when the emission of a cathode

\* With smaller oxygen pressures a state seems to be reached such as also occurs during emission; cf. W. Espe, *Wiss. Ver. Siemens-Konz.* 5, 3es Heft, 57 (1927).

† A. L. Reimann and R. Murgoci, *Phil. Mag.* 9, 440 (1930).

‡ M. Benjamin and H. P. Rooksby, *Phil. Mag.* 15, 810 (1933).

covered with a single oxide, thus no mixture of barium and strontium oxides, is poisoned by oxygen, it may always be completely recovered. With the use of a mixture of barium oxide and strontium oxide, however, a change in the composition takes place during the re-activation, since barium oxide evaporates much more easily than strontium oxide even from mixed crystals with strontium oxide.\* A change in the composition of the mixed crystals BaO, SrO may result in a considerable change in the emission. In Fig. 144 the emission at 1020° K. is given as a function of the composition of the oxide mixed crystal. After heating at a high temperature, which is necessary for the re-activation after poisoning, the original emission can no longer be recovered, due to the preferential loss of barium oxide, when the most favourable mixture was originally chosen.

As we have already seen in § 101, the cathodes may also be de-activated by evaporation of the adsorbed barium at a temperature of about 1600° K. As might be expected on the grounds of the view here developed, in a partial de-activation in this manner not the  $\phi_i$  but the  $A_i$  of the emission formula is changed, and in fact decreased.† If one heats for a relatively short time at 1400° K. the surface of the cathode but not the layer throughout its whole thickness loses barium; a short heating at 900 to 1000° K. restores the emissivity, due to the diffusion of barium atoms to the outside. If too much barium is evaporated the normal emission can be restored by electrolytic reactivation. Mixed crystals of barium and strontium oxides again give difficulties in this respect because of the more rapid evaporation of the barium oxide.

\* Cf. A. Claassen and C. F. Veenemans, *Z. Phys.* **80**, 342 (1933).

† W. Espe, *Wiss. Ver. Siemens-Konz.* **5**, 3es Heft, 43 (1927).

## CHAPTER XV

### THE EMISSION OF ELECTRONS INTO INTERMEDIATE LAYERS OF DIELECTRICS AND INTO BLOCKING LAYERS

#### § 107. Photoelectric emission from adsorbed metals into a dielectric layer.

Atoms which are adsorbed on an external surface of a dielectric may be ionized by the absorption of light (Chap. ix) as well as by the increase of temperature (Chap. xiv). If the electrons freed in this way are emitted to the outside we are concerned with photoelectric or thermionic emission. Atoms which are adsorbed on an internal surface within a salt lattice may also be ionized by light (Chap. x) as well as by increase of temperature (Chap. xi). The electrons in this case are emitted into the salt lattice, and we are concerned with the phenomena of photoelectric conduction and electronic semi-conduction.

One may now ask whether atoms which are adsorbed on an external surface are also able, on ionization, to emit their electrons toward the inside, that is, into the salt lattice. This possibility actually does exist.

In § 82 we became acquainted with the thermal ionization of adsorbed alkali metal atoms accompanied by the penetration of the emitted electrons into a dielectric. There we saw that the additive coloration of alkali halides when they are heated in the vapour of alkali metals does not depend upon an actual diffusion of alkali metal atoms, but upon a diffusion of electrons. The atoms adsorbed on the crystal emit their electrons thermally into the lattice, where these electrons are captured by alkali metal ions which are situated on internal surfaces. As we have already mentioned in § 82 these electrons may continue their course through the lattice in a similar manner: the internally adsorbed atoms formed lose their electrons in turn by thermal ionization and the electrons may then pass on to a following ion on an internal surface, and so

on. At the same time we also saw in § 82 that as a result of the space charges formed, the positive ions left behind move ahead in the lattice, so that electric neutrality is sought by means of electrolytic transport of material.

In the case of photoelectric phenomena also, electrons which are emitted by adsorbed atoms may penetrate into lattices of dielectrics. When a metal plate is covered with a thin layer of a salt, and alkali metal atoms are adsorbed on this salt layer, a system is obtained in which, upon illumination, electrons move from the alkali metal through the salt lattice to the metal plate.\* Salt films, such as may be obtained by sublimation, are very suitable for this purpose. In § 59 we saw that such salt layers serve very well as adsorbent surfaces. Such a surface as a whole is already thin ( $0.1$  to  $0.2\ \mu$ ), but in addition it con-

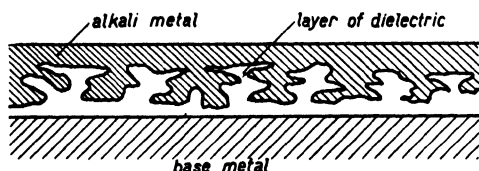


Fig. 145. Diagram of an electrode system in which one of the metal electrodes is adsorbed on a dielectric intermediate layer.

sists of very thin laminae. If one allows alkali metal to be adsorbed and then an excess to condense on the surface, one obtains a system of two metal electrodes (Fig. 145) which are separated by a layer of a dielectric. The effective separation of the alkali metal electrode and the other metal electrode is given by the average thickness of the laminae of the salt. With calcium fluoride layers for example this may be (§ 59)  $0.25 \times 10^{-6}$  cm., so that the electrons emitted by the adsorbed alkali metal upon illumination have only to cover a very short distance through the salt in order to reach the other electrode. The result is that under continual, constant illumination a continual, constant photocurrent is obtained. If silver is taken as a base metal, calcium fluoride as a salt layer and caesium as photoelectric adsorbed metal, such a photoelectrically sensitive system is obtained. Another example is the following

\* J. H. de Boer and W. Ch. van Geel, *Physica*, **1**, 449 (1934).

combination: a zirconium plate is superficially oxidized (electrolytically for instance) to give a layer of zirconium oxide ( $\text{ZrO}_2$ ) of from  $0.1$  to  $1\ \mu$  thickness. Upon this zirconium oxide layer caesium is adsorbed, which, together with an excess of condensed caesium, in order to form a good contact connection with the outside, forms the photoelectrically active cathode. The combination,\* sodium covered with sodium oxide upon which more sodium is adsorbed, also forms a photoelectric system which acts according to the principles sketched above.

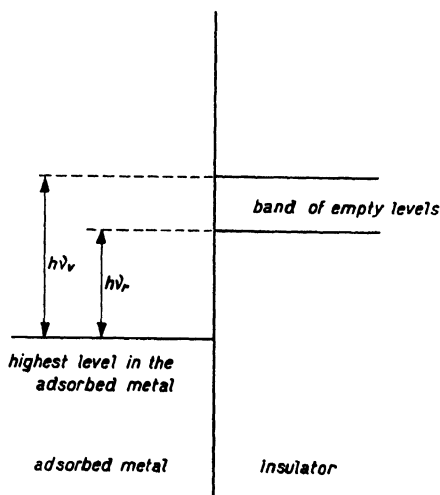


Fig. 146. In the emission of electrons from an adsorbed metal into a dielectric there is a violet ( $h\nu_v$ ) as well as a red ( $h\nu_r$ ) threshold.

The photocurrent obtained at a definite illumination is smaller the thicker the dielectric layer. However, easily measurable, constant photocurrents can be obtained with intermediate layers of  $100\ \mu$  thickness in the combination: nickel as base metal, barium oxide as dielectric, and barium as adsorbed, photoelectrically active electrode. Quite different substances also, such as artificial resins, may be used as the dielectric layer.

The red threshold of the spectral sensitivity distribution of the photoelectric effect is given by the energy difference  $h\nu_r$ , between the highest energy level in the adsorbed metal (Fig.

\* P. Selényi, *Physica*, 1, 781 (1934).



146) and the lowest energy level of the normally empty band of the insulator (cf. for example § 85). There must be not only such a red threshold but also a violet limit, whose position is given by the energy difference  $h\nu_0$ , between the highest energy level in the adsorbed metal and the highest energy level of the normally empty band of the insulator. Preliminary observations have actually indicated that in this effect there is practically a symmetrical spectral sensitivity curve, whose maximum for the system Zr-ZrO<sub>2</sub>-Cs for example lies at about 5800 Å.

The photocurrent discussed above flows upon illumination of the electrode system without a potential difference being applied between the electrodes. If the photoelectric cathode is made negative with respect to the other electrode, the current increases. It is possible to use only low voltages, e.g. about two volts in the case of a zirconium oxide layer on zirconium, because otherwise a breakdown occurs and the photocurrent disappears.

### § 108. Electron emission into a dielectric layer by means of strong fields.

The fact that one of the electrodes (the alkali or alkaline earth metal) is adsorbed on the dielectric intermediate layer results in the fact that, even at ordinary temperatures and without illumination, the electrons pass much more easily from the adsorbed electrode through the intermediate layer to the other electrode than in the opposite direction. The electrode system of the two metals which are separated by a thin dielectric layer and one of which metals is adsorbed on the surface of the dielectric has thus rectifying properties.\* The explanation of this phenomenon must be sought in the emission of electrons by means of strong fields (§ 9). If we again take as an example a silver surface on which a thin film of calcium fluoride is deposited, on which surface caesium or potassium is adsorbed, we obtain once more an electrode system in which the two metal electrodes are separated from

\* J. H. de Boer and W. Ch. van Geel, *Physica*, 2 (1935), April number

each other by only about  $10^{-5}$  to  $10^{-6}$  cm. (the average thickness of the laminae, § 59). Thus when a tension of 1 volt is applied there is already a field of  $10^5$  to  $10^6$  volts/cm., if the electrodes are perfectly plane. This is an electric field strong enough to give an appreciable cold electron emission. The alkali or alkaline earth metal is, however, adsorbed on the surface, that is to say it makes an ideal contact with the surface and it follows the surface in all its deviations from the perfect plane. Thanks to the laminary structure of the salt surface, or, in general, thanks to the relatively porous surface structure of every substance built up of ions, the adsorbed metal electrode is provided with many fine points (the hollows and cracks in the dielectric which the metal fills) on which a much stronger electric field dominates than on a plane surface. Therefore, if the adsorbed electrode is made negative, a strong electron current will flow through the dielectric, thanks to the cold electron emission resulting from the strong electric fields at the points. If the nonadsorbed electrode is made negative, then there are less strong electric fields concerned and a much weaker electron current flows through the dielectric.

When the intermediate layer is a thin layer of calcium fluoride or potassium chloride or a similar salt, and the adsorbed electrode is caesium or potassium, a short-circuit easily occurs if this electrode is made negative. In this case one must assume that fine needles of calcium or potassium have been formed; the atoms which constitute these needles or bridges result from the neutralization of the positive ions of the salt layer by electrons which are stuck in this layer and perhaps from an electrolytic component of the current through the layer.\* After such a short-circuit the resistance in this direction is given solely by Ohm's law (see line *a* in Fig. 147). If the current is reversed a strong current also flows through the intermediate layer for a short time and there is no rectifying

\* For this latter case cf. A. F. Joffé, *The Physics of Crystals*, p. 93, McGraw Hill Book Co. Inc., New York and London (1928); C. Tubandt in *Handbuch der Experimentalphysik* (Wien-Harms), Leipzig, 12, 1, pp. 384 ff. (1932).

action at all (line  $b'$  in Fig. 147).<sup>\*</sup> After a very short time, however, which is longer according as the adsorbed electrode was previously negative during a longer time, the easily conducting state caused by the short-circuit is terminated and a current-potential relation is obtained as is represented by line  $b$  in Fig. 147.<sup>†</sup> Line  $b$  has the character of a saturation curve. This indicates that here a conductivity of the layer itself—probably as a result of internally adsorbed alkali or alkaline earth metal atoms formed by electron diffusion—plays a part. The saturation is caused by the fact that the average distance which the electrons cover in the field (this distance increases

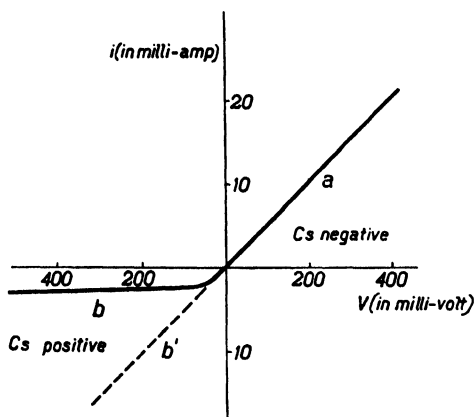


Fig. 147. Current-potential relation of a Ag-CaF<sub>2</sub>-Cs system.

of course with the field, see § 76) reaches the same value as the thickness of the salt layer itself.

If other intermediate layers are chosen, zirconium oxide, magnesium oxide, calcium oxide, or a combination of a silicon dioxide layer with an additional salt layer deposited on it, or a layer of a resin or of sulphur or phosphorus with a salt layer

<sup>\*</sup> In the electrolysis of thin plates of salt crystals between two metallic electrodes a strong polarization tension very often occurs (cf. A. F. Joffé, *The Physics of Crystals*, foot-note<sup>\*</sup> on p. 371). J. G. W. Mulder (unpublished) found such a polarization tension when using thin salt layers, obtained by sublimation, between two nonadsorbed metal contacts. In the case under consideration such a polarization tension was not observed.

<sup>†</sup> J. H. de Boer and W. Ch. van Geel, *Physica*, 2 (1935), April number.

upon it (the adsorbed electrode is then adsorbed in each case on the salt layer), a short-circuit or an electrical breakdown is obtained much less easily.\*

The current-potential curves may be represented by formulae which are in agreement with the character of the strong field emission. Namely, if the adsorbed electrode is positive and the emission takes place, therefore, from the non-adsorbed electrode through the dielectric double layer to the adsorbed electrode, the following formula holds for the current-potential curve (curve *b* in Fig. 148):

$$i = ce^{-\frac{k}{V}},$$

where *i* is the current, *V* the applied potential and *c* and *k* are constants. If on the other hand the adsorbed electrode is made negative:

$$i = CV^{\frac{3}{2}},$$

where *C* is a constant.

We have seen in § 9 that for electron emission in strong fields the following formula is valid:

$$i = aE_f^2 e^{-\frac{b}{E_f}},$$

where *E<sub>f</sub>* is the electric field and *a* and *b* are constants. For relatively small values of *E<sub>f</sub>* and large values of *b* (adsorbed electrode positive) the formula is dominated by the power of *e*; for very large values of *E<sub>f</sub>* and small values of *b*, however, it is dominated by the quadratic term. The fact that in this last case no quadratic term, but a 3/2 power, is found must be ascribed to the formation of space charges.

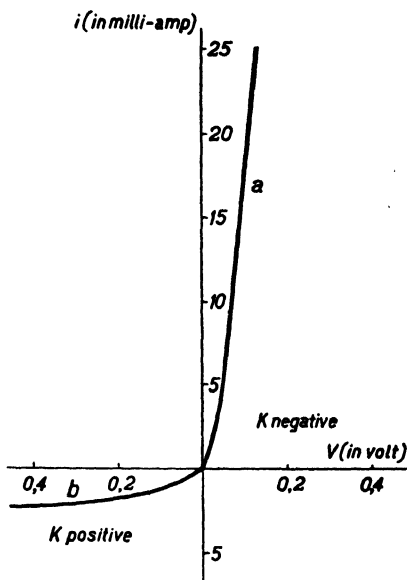


Fig. 148. Current-potential relation of a Ag-resin- $\text{CaF}_2$ -K system.

\* W. Ch. van Geel and J. H. de Boer, *Physica*, 2 (1935), April number.

The whole behaviour of these electrode systems indicates in any case that we are here concerned with cold emission of electrons, whereby the field in one direction is much stronger than in the other, which is brought about by the fact that one of the electrodes is adsorbed.

Clausing\* made a metallic contact on the outside of an oxide-coated filament and found that electrons pass more easily from that contact through the oxide layer to the base metal than in the reverse direction. In this case we may assume the adsorbed barium atoms (Chap. XIV) to be the adsorbed electrode.

### § 109. Dry rectifiers.

The distinguishing feature of the phenomena discussed in §§ 107 and 108 was that an electron current can be obtained through the dielectric layer much more easily in one direction (from the adsorbed electrode to the nonadsorbed electrode) than in the other direction. Such a rectifying action, thanks to the presence of an intermediate dielectric layer, is also present in the case of the well-known crystal detectors, such as can be used in radio technique, and is also present in the case of the so-called dry rectifiers, where a blocking layer is present. The rectifying action of a metal contact on many semi-conducting crystals occurring in nature has long been known, as well as the rectifying action of many metallic oxide layers developed on metals.† In the investigations of recent years it appears that in all these cases we are concerned with an electrode system consisting of a metal and a semi-conductor which are separated from each other by a blocking layer. A more detailed discussion of these electrode systems would be outside the scope of this book, and we shall thus confine ourselves to a brief statement of the construction and the principles of action, while reference is made to other surveys for further details.‡ Many experiments have been carried out in recent years on the rectifying action of a layer of cuprous oxide

\* P. Clausing (unpublished).

† F. Braun, *Ann. Phys.*, Lpz., 1, 95 (1877); 4, 476 (1878).

‡ Cf., for example, L. O. Grondahl, *Rev. Mod. Phys.* 5, 141 (1933).

( $\text{Cu}_2\text{O}$ ) which has been obtained upon copper by oxidation.\* For this purpose a plate of copper is heated in air or oxygen to above  $1000^\circ\text{C}$ . The copper plate covered with cuprous oxide may afterwards be cooled in two ways: (a) by rapid immersion in cold water, (b) by allowing it to cool slowly in air. The first method of cooling gives cuprous oxide with a relatively low resistance, the second gives the oxide with a high resistance. In both cases the resistance is still too high. In order to decrease this resistance the rectifier is heated for some time in an oven at  $500\text{--}600^\circ\text{C}$ . in the presence of air (oxygen). Oxygen

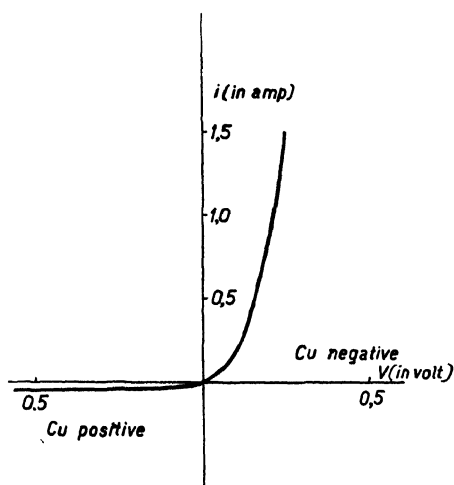


Fig. 149. Current-potential relation in a copper-cuprous oxide rectifier.  
O. v. Auwers and H. Kerschbaum, *Ann. Phys., Lpz.*, **7**, 170 (1930).

is taken up by the cuprous oxide and its resistance is thereby lowered (§ 91). The difference in resistance due to the differing methods of cooling continues to exist in the final product. A thin layer of cupric oxide ( $\text{CuO}$ ) present on the surface is removed. If a contact (a wire gauze for instance) is fixed upon the cuprous oxide, a rectifying system is obtained whereby the electrons easily pass from the basic copper to the oxide and with difficulty in the opposite direction (Fig. 149).

Schottky and Deutschmann† assume that there is a poorly conducting or an insulating blocking layer between the copper

\* L. O. Grondahl, *Science*, **64**, 306 (1926).

† W. Schottky and W. Deutschmann, *Phys. Z.* **30**, 839 (1929).

and the cuprous oxide formed upon it, the thickness of which layer they have provisionally estimated to be from  $3 \times 10^{-6}$  to  $3 \times 10^{-8}$  cm. by means of capacity measurements. It has been proved by Schottky and his collaborators\* that a rectifying system can also be obtained by depositing a metallic layer or a layer of graphite on a massive cuprous oxide plate. In this case the electrons pass more easily from the deposited metal to the cuprous oxide than in the opposite direction, and it must again be assumed that there exists a blocking layer between the deposited metal and the cuprous oxide or that such a layer has been formed. Such a layer is actually not always formed; practically no rectifying action is obtained if the surface of the cuprous oxide is first cleaned by a mechanical treatment. Chemical etching, however, is not at all unfavourable to the production of the rectifying action. If silver or gold as a metal electrode is sublimed in a vacuum, while at the same time the cuprous oxide is kept at a low temperature (room temperature or better  $-180^{\circ}\text{C.}$ ), again no rectifying action is obtained. On the other hand if the cuprous oxide surface is first bombarded by electrons or by ions (any kind of ions will do), one obtains immediately after sublimation of silver or gold a rectifying system.† Obviously a chemical reaction takes place here, whereby a layer of cuprous oxide is probably formed which is wholly or for the greater part freed of its superfluous oxygen. Waibel and Schottky determined by etching tests that this layer is about  $5 \times 10^{-6}$  cm. thick. In § 91 we saw that the conductivity of a semi-conductor such as cuprous oxide can be the result of the taking up in the lattice of superfluous oxygen; pure cuprous oxide is either an insulator at room temperature or has at the most a very small conductivity ( $10^{-9}$  ohm $^{-1}$  cm. $^{-1}$ ).

The assumption that the blocking layer is formed by a thin layer of pure cuprous oxide, which contains no excess oxygen or copper, is confirmed by experiments by Rother and Bomke‡ on

\* Cf. E. Duhme and W. Schottky, *Naturwissenschaften*, **18**, 735 (1930).

† F. Waibel and W. Schottky, *Naturwissenschaften*, **20**, 297 (1932).

‡ F. Rother and H. Bomke, *Z. Phys.* **81**, 771 (1933); *Phys. Z.* **34**, 865 (1933).

the reactions which take place during the oxidation of copper. In the oxidation of copper not only do copper atoms diffuse through the cuprous oxide layer already formed to be oxidized on the surface, but also, and especially at the high temperature (over  $1000^{\circ}\text{C}.$ ) at which oxidation is carried out, oxygen diffuses through the cuprous oxide film already formed to the inside and there oxidizes copper. The result is that there is a zone immediately contiguous to the copper in which oxygen has penetrated into the copper lattice, next to which zone there is a

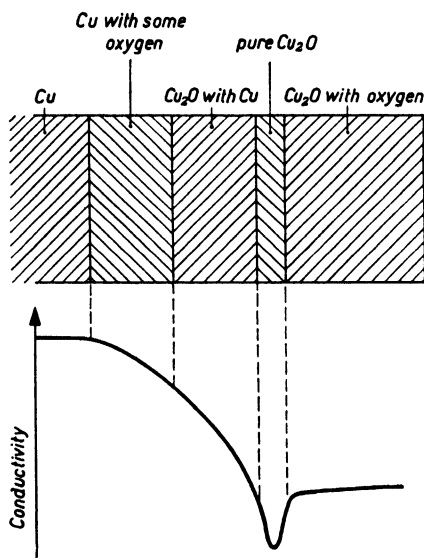


Fig. 150. Different layers on oxidized copper and a diagram of the conductivity. F. Rother and H. Bomke, *Z. Phys.* **81**, 733 (1933).

region of cuprous oxide with excess copper. Following next to this region is a very thin layer of pure cuprous oxide, and thereafter a layer of cuprous oxide which has taken up excess oxygen (Fig. 150). The first zone, which may be considered as copper contaminated with oxygen, still has a metallic conductivity; the following zone is a semi-conductor, then follows the blocking layer (the pure cuprous oxide), whereupon follows the semi-conducting cuprous oxide layer with excess oxygen. From experiments on the dependence of the conductivity of the blocking layer itself on temperature, it appears that the



work necessary to free an electron in the blocking layer is the same as in pure cuprous oxide.\*

Such an insulating blocking layer is also present in other similar rectifying systems. In many dry rectifiers where selenium is used as a semi-conductor this layer consists of some metal selenide. The layer is formed during the deposition of the selenium on a metal base between this metal and the semi-conductor, or it is formed on the selenium from the impurities contained in it. A second electrode is afterwards deposited on this blocking layer. In the case of silicon carbide detectors, the blocking layer consists of a layer of silicon dioxide about  $10^{-5}$  cm. thick.† Instead of allowing the blocking layers to be formed more or less accidentally one may also voluntarily first deposit an insulating film of the desired thickness on a metal, and then deposit the semi-conductor upon it. In this manner van Geel provides metals such as aluminium, tantalum, zirconium and magnesium with an oxide film either by oxidation in air or by electrolytic oxidation, and then deposits semi-conductors such as copper sulphide ( $\text{Cu}_2\text{S}$ ) or copper iodide ( $\text{CuI}$ ).‡ The thickness and resistance of the blocking layer can be regulated very accurately if the blocking layer has no chemical relation with one of the electrodes, but consists of an entirely arbitrary insulating layer. For example, a layer of quartz may be deposited on the semi-conductor cuprous oxide,§ and upon the quartz a gold electrode, or blocking layers may also be used which consist of salt layers obtained by sublimation, artificial resins, paper, etc.||

In all the cases discussed above the rectifying system consists of a metal and a semi-conductor which are separated from each other by a blocking layer (in the case of the  $\text{Cu}_2\text{O}$  rectifier there is a semi-conductor between this blocking layer and the metal),

\* W. Ch. van Geel, *Physica*, 1, 1143 (1934).

† O. W. Lossew, *Phil. Mag.* 6, 1024 (1928); *Phys. Z.* 30, 920 (1929); B. Claus, *Ann. Phys.*, Lpz., 11, 331 (1931); 14, 644 (1932); P. Specht, *Z. Phys.* 90, 145 (1934).

‡ W. Ch. van Geel, *Z. Phys.* 69, 775 (1931).

§ W. Jusé, *Nature*, Lond., 132, 242 (1933).

|| W. Ch. van Geel, *Nature*, Lond., 132, 711 (1933).

in which system the electrons always pass most easily from the metal, via the blocking layer, to the semi-conductor. In order to explain this last fact various possibilities have been proposed.\* The most probable explanation is, however, that the electron current through the blocking layer is created by electron emission under the influence of strong fields,† just as was the case with the systems discussed in the previous section. The great difference is that with the systems now under consideration the principal part is not played by the fact that the electric field is so much stronger in one direction (thanks to the action of the points of the adsorbed electrode), but the essential fact that there are so many more electrons available in the metal electrode than in the semi-conductor is here the cause of the rectification. From the side of the metal electrode all of the conduction electrons which reach the border of the blocking layer can contribute to the cold emission into that layer. From the side of the semi-conductor, however, only those electrons are available which can be emitted by the internally adsorbed atoms or impurities, thus a much smaller number. It is obvious that if in addition an increased field action can be obtained by adsorption on the surface of the blocking layer, the rectification can thereby be increased.

The current-potential characteristics agree with this conception. They can be represented either by the formula

$$i = c V^2 e^{-\frac{k}{V}}$$

or by

$$i = C V^{\frac{3}{2}}$$

(see § 108).‡

### § 110. Photoelectric cells with blocking layers.

A system of electrodes consisting of a metal and a semi-conductor in which electrons may be liberated by the action of light, the two separated by a blocking layer, has not only

\* Cf. J. Frenkel and A. Joffé, *Phys. Z. Sowjet.* 1, 60 (1932); D. N. Nasledow and L. M. Nemenow, *Phys. Z. Sowjet.* 2, 128 (1932); R. H. Fowler, *Phys. Z. Sowjet.* 3, 526 (1933).

† W. Ch. van Geel, *Z. Phys.* 69, 765 (1931); W. Ch. van Geel and H. Emmens, *Z. Phys.* 87, 220 (1933).

‡ W. Ch. van Geel, *loc. cit.*; P. Specht, *Z. Phys.* 90, 145 (1934).

rectifying properties (see previous section), but it is also photoelectrically sensitive. When the limiting layer between the blocking layer and the semi-conductor is illuminated—without a potential being applied between the electrodes—a current passes through the system. If the two electrodes are not connected through an external circuit, an electromotive force is created upon illumination. If the circuit is closed a current flows which is smaller the greater the resistance in the external circuit.

The photoelectric properties of cuprous oxide rectifiers were discovered by various investigators independently of each other.\* When cuprous oxide is formed by oxidation on a copper plate and a metal gauze is fixed to the cuprous oxide as further contact, a photoelectric cell is obtained in which an electron current flows upon illumination from the cuprous oxide to the copper base upon which the oxide is formed. The striking fact in this connection is that the electrons liberated during the illumination pass in a direction which is opposite to that in which they pass most easily according to the rectifying action. It appears from very detailed and elucidating experiments by Schottky and his coworkers† that the photoelectrons are freed in the semi-conductor, and moreover at the border between semi-conductor and blocking layer. These electrons are emitted into the blocking layer and reach the metal electrode through it. They then continue as photocurrent through an external connection back to the semi-conductor again, if the external resistance is not too great, and if the illumination takes place close to the contact fixed upon the semi-conductor. If, however, the external resistance is large or if the illumination is at a certain distance from the contact on the semi-conductor, whereby a certain resistance of the semi-conductor is introduced into the path of the electrons flowing back into it from the external connection, then all or

\* L. O. Grondahl, *Science*, **36**, 306 (1926); B. Lange, *Phys. Z.* **31**, 139, 964 (1930); W. Graffunder, *Phys. Z.* **31**, 375 (1930).

† W. Schottky, *Phys. Z.* **31**, 913 (1930); *Z. techn. Phys.* **11**, 458 (1930); W. Schottky in collaboration with E. Duhme, O. v. Auwers and H. Kerschbaum, *Naturwissenschaften*, **18**, 735 (1930).

a part of the electrons which have penetrated through the blocking layer return again through the blocking layer to the semi-conductor, and little or no photocurrent is observable.

In the above-described combination the blocking layer is situated between the cuprous oxide and the copper, and the light must pass through the cuprous oxide layer in order to free photoelectrons. Since the blocking layer is situated here behind the semi-conducting layer, these cells are sometimes given the German name "Hinterwandzellen". In the previous section we saw that dry rectifiers could also be obtained by depositing a metal layer on cuprous oxide. If a thin transparent metallic film is chosen for this purpose and care is taken that a blocking layer is formed between this transparent metal layer and the semi-conductor, so-called "Vorderwandzellen" are obtained. The spectral distribution of the sensitivity of these photocells is given not only by the quantity of energy necessary to emit electrons from the semi-conductor into the blocking layer, but also by the layers of the semi-conductor acting as spectral light filters (in the case of the Hinterwandzellen) or by layers of the thin metal electrode (in the case of the Vorderwandzellen). The Vorderwandzellen are more sensitive than the Hinterwandzellen and can be made with semi-conductors which are less transparent than cuprous oxide, as for example selenium.\*

The primary phenomenon in these photocells with a blocking layer is the photocurrent passing through the blocking layer. This is proportional to the light intensity,† and is free of time lag when no tension is applied between the electrodes. In addition the direct photocurrent is probably also very little dependent on temperature. The great dependence on temperature observed in photocells with blocking layers,‡ the dependence on potential applied, etc., are probably caused chiefly by secondary phenomena and not by variations in the

\* B. Lange, *Naturwissenschaften*, **19**, 527 (1931); L. Bergmann, *Phys. Z.* **32**, 286 (1931).

† O. von Auwers and H. Kerschbaum, *Ann. Phys.*, Lpz., **7**, 129 (1930).

‡ H. Teichmann, *Z. Phys.* **67**, 192 (1931); B. Lange, *Phys. Z.* **32**, 850 (1931).

true photocurrent.\* The dependence of the photocurrent of cuprous oxide cells on temperature is caused in part also by the dependence of the resistance of the blocking layer on temperature.†

It is striking, as has already been mentioned above, that while during the action as dry rectifier the most favourable direction for the passage of electrons is the one where the electrons pass from the metal through the blocking layer to the semi-conductor, during the action as photocell the electrons flow against the blocking direction, that is, from the semi-conductor, via the blocking layer to the metal electrode. In this respect the electrode systems, semi-conductor—blocking layer—metal, differ from the electrode systems discussed in §§ 107 and 108, consisting of two metals and an intermediate dielectric layer upon which one of the metals is adsorbed. In this latter case the electrons always pass more easily from the adsorbed electrode through the dielectric layer to the non-adsorbed electrode, and this is also the direction of the electrons in the photocurrent. The reason for the different behaviour of the system with a semi-conductor must be sought in the fact that in the absorption of light at the limiting plane between semi-conductor and blocking layer each light quantum absorbed there frees an electron, and half of these electrons are emitted into the blocking layer. In the opposite metal electrode, however, we are again concerned with conduction electrons, a very small percentage of which are emitted by the absorption of light.‡ We are thus in principle here again concerned with a phenomenon similar to that which takes place in the selective photoeffect (cf. for instance §§ 65 and 66), where each quantum absorbed leads to ionization, while in the normal photoelectric emission only very few absorbed quanta give rise to emitted electrons.

Although the principle of the action of these photocells with blocking layers can be understood, a number of details remains

\* W. Schottky, *Phys. Z.* **32**, 833 (1931); F. Waibel and W. Schottky, *Phys. Z.* **33**, 583 (1932).

† W. Ch. van Geel, *Physica*, **1**, 1143 (1934).

‡ R. H. Fowler, *Proc. Camb. Phil. Soc.* **30**, 55 (1934).

which can be explained qualitatively and formally, but of which our knowledge is still too slight, while there are also many quite obscure points remaining.\*

Further treatment of these phenomena would lead too far afield, so that we must again refer the reader to other surveys for these photoelectric† phenomena.

If we again briefly compare the principles of the action of the systems of electrodes treated in §§ 107, 108, 109 and 110, we may make the following table:

	Metal—dielectric layer— adsorbed metal	Metal—blocking layer— semi-conductor
With applied potential	Electron current due to cold emission (high field) Electron current greatest when adsorbed metal is negative (points on the surface)	Electron current due to high field Electron current greatest when metal is negative (metal has many more available electrons than semi-conductor)
Upon illumi- nation	Electron current from adsorbed metal (usually lower work function) through dielectric layer to other metal Selective emission from adsorbed metal	Electron current from semi-conductor through blocking layer to metal  Selective emission from internally adsorbed atoms of the semi- conductor

We shall conclude with two observations:

(1) When the semi-conductor of the system, metal—blocking layer—semi-conductor, is replaced by an electrolyte the phenomena of electrolytic rectifiers come into force, and with a suitable choice of electrode material and electrolyte, photoelectrically sensitive systems (photovoltaic effects, Becquerel effects) are obtained.

\* Cf. W. Ch. van Geel, *Physica*, 1, 531 (1934).

† A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, pp. 361 ff. (1932); R. Fleischer and H. Teichmann, *Die Lichtelektrische Zelle*, Theodor Steinkopff, Dresden and Leipzig, pp. 138 ff. (1932); G. Liandrat, *Revue Générale de l'Électricité*, 35, 415, 467 (1934).

(2) In the illumination of semi-conductors from one side only a potential difference is created (the side away from the light becomes negative).<sup>\*</sup> This has nothing to do with the formation of blocking layers, the phenomenon is brought about by a decline in concentration of freed electrons. Since the intensity of the light decreases with the depth to which it has penetrated, fewer and fewer electrons are freed in the direction of the beam of light. From the side which receives more light, more electrons diffuse to the less intensely illuminated side than the other way round, whereby the potential difference is created.

<sup>\*</sup> H. Dember, *Phys. Z.* **32**, 554, 856 (1931); **33**, 207 (1932); H. Teichmann, *Z. Phys.* **78**, 21 (1932); L. Bergmann, *Phys. Z.* **33**, 209 (1932).

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